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Lanthanide-Containing Molecular and Supramolecular Polymetallic Functional Assemblies

Jean-Claude G. Bünzli*,† and Claude Piguet*,‡

Institute of Molecular and Biological Chemistry, Swiss Federal Institute of Technology, BCH 1402, CH-1015 Lausanne, and the Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

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I. Introduction

As a result of the different degrees of stabilization experienced by the 4f, 5d, and 6s orbitals occurring upon ionization of the neutral metal, the lanthanides (La−Lu, $Z = 57-71$) exist almost exclusively in their trivalent state Ln(III) ([Xe]$4f^n$, $n = 0-14$) in coordination complexes or supramolecular assemblies.[1] Except for some arene compounds involving bulky substituted benzenes or cyclo-octatetraenes,[2] covalence plays a minor role in Ln−ligand dative bonds and the nature of the coordination sphere is controlled by a subtle interplay between electrostatic interactions and interligand steric constraints.[3] Variable coordination numbers ($6 \leq \mathrm{CN} \leq 12$) and geometries are thus observed in lanthanide complexes, leading to limited success in the design of molecular architectures with predetermined structures.[3,4] Although rigid or semirigid receptors may help to control the coordination sphere according to the *lock-and-key* and *induced fit* concepts,[5] detailed studies of lanthanide solvates with water or acetonitrile suggest that trivalent lanthanides display a tendency to adopt nine-coordinate tricapped trigonal prismatic (TTP) arrangements around the metal ion in the solid state. In solution, the picture is a little more subtle:[6] in water, for instance, large Ln(III) ions at the beginning of the series (Ln = La−Nd) adopt TTP geometries, which are gradually transformed into eight-coordinate square antiprismatic (SAP) arrangements for small Ln(III) ions (Ln = Tb−Lu), equilibria between CN = 8 and CN = 9 being observed for Ln = Nd−Tb.[7] The systematic contraction of the ionic radii observed when going from Ln = La to Lu (often referred to as the lanthanide contraction)[8] explains this trend and increases electrostatic bonding for heavier lanthanides, but this variation is so smooth and limited (15% contraction between La and Lu and ≈1% between two successive lanthanides) that selective recognition and incorporation into organized supramolecular architectures remains challenging.[5] A rational access to extended polymetallic lanthanide-containing assemblies with predictable and controlled geometries is consequently very limited, and pioneer work in this field has focused on poorly characterized intricate mixtures of complexes in solution which are ‘transformed’ into well-defined solid-state clusters or networks through crystallization processes involving a rich palette of

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† Institute of Molecular and Biological Chemistry, Lausanne. E-mail: Jean-Claude.Bunzli@epfl.ch.

‡ Department of Inorganic, Analytical and Applied Chemistry, Geneva. E-mail: Claude.Piguet@chiam.unige.ch.

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Jean-Claude Bünzli earned his Ph.D. degree at the Swiss Federal Institute of Technology (Lausanne) in 1971. He spent two years at the University of British Columbia (photoelectron spectroscopy) and one year at the Swiss Federal Institute of Technology in Zürich (physical organic chemistry) as a teaching postdoctoral fellow. Since 1980 he has been acting as Full Professor at the University of Lausanne, where he pursues a research program on the coordination and spectrochemistry of lanthanide ions, with particular interest in the relationship between structure and luminescent properties and in the design of supramolecular luminescent probes.

Claude Piguet studied chemistry at the University of Geneva and received his M.S. degree in Chemistry in 1986 and his Ph.D. degree with felicitations in 1989 in the field of biomimetic copper–dioxygen complexes. After postdoctoral periods in the group of Professor J.-M. Lehn, Professor A. F. Williams, and Professor J.-C. G. Bünzli, he initiated research projects in the field of the supramolecular chemistry of lanthanide-metal ions. In 1995 he received the *Werner Medal* of the New Swiss Chemical Society for these contributions and the *Werner* grant. He was an Assistant Professor at the University of Geneva in 1995–1998 and was appointed in 1999 as Full Professor of Inorganic Chemistry. His research interests and topics include the design of self-assembled functional supramolecular complexes with d-block and f-block metal ions, the preparation of lanthanide-containing metallomesogens, the development of paramagnetic NMR, and the exploration of weak interactions in metallosupramolecular chemistry.

intermolecular interactions.[9] Although many efforts have been made to produce discrete polymetallic s–f,[10,11] d–f,[11–13] and f–f[14–18] assemblies whose solid-state structures at least partially reflect solution structure and speciation, it is only recently that the need for 'magnetically isolated' dimetallic complexes has taken advantage of the stereochemical preferences of appended d-block ions associated with steric constraints induced by the ligands and the counterions to provide discrete solid-state assemblies in which electronic, spectroscopic, and magnetic properties are protected from intermolecular perturbations.[12,19,20] Reliable modeling of intermetallic magnetic communications in d–f pairs[21,22] and close control of intermetallic d–f[23] and f–f[24] energy transfers result, but we ask the question 'why so much effort for producing chemical curiosities with the ultimate goal of refining modeling of intermetallic magnetic and multipolar interactions?' A tentative answer is intrinsically contained in the peculiar $4f^n$ open-shell configuration of Ln(III) ions in which the 4f orbitals are screened from external perturbations by outer filled $5s^2$ and $5p^6$ shells (Figure 1b). The 4f electrons thus retain the fascinating magnetic and spectroscopic properties of the free ions which can be finely tuned in a predictable way via a close control of the metallic coordination sphere in the complexes.[1,25] Among a wealth of stimulating applications, the recent developments of (i) new phosphors for lighting,[26] (ii) high-efficiency electroluminescent devices for light-emitting diodes,[27] (iii) contrast agents for medical magnetic resonance imaging,[28] (iv) luminescent probes for analytes,[29] (v) labels for proteins and amino acids,[30] (vi) light-emitting sensors in fluoroimmunoassays,[31] (vii) tags for time-resolved luminescence microscopy,[32] (viii) magnetically addressable liquid crystals,[33] (ix) magnetic alloys for refrigeration,[34] (x) precursors for superconducting materials,[35] (xi) specific redox reagents for chemical transformation[36] or molecular-based information storage,[37] and (xii) acidic catalysts for sophisticated organic transformations[38,39] or for the cleavage of

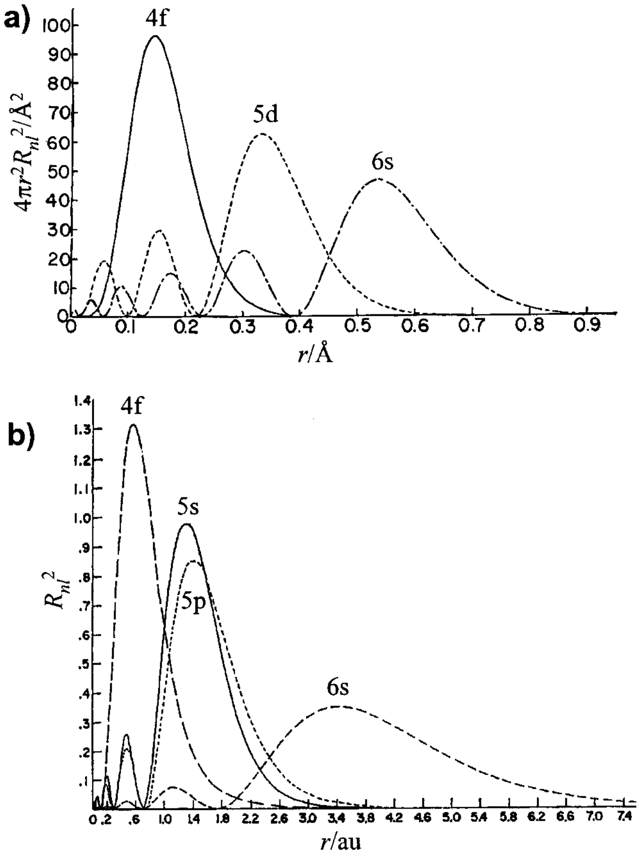


Figure 1. Radial parts of the hydrogenic orbitals plotted as (a) the probability of finding an electron at the distance *r* from the nucleus for the 4f, 5d, and 6s orbitals of cerium (adapted from ref 43a) and(b) the radial charge densities for the 4f, 5s, 5p, and 6s orbitals of Gd(I) (adapted from ref 43b).

phosphodiester bridges in RNA[40] fully justify the efforts made to control the metallic sites and to selectively introduce lanthanides into organized assemblies. For more than two decades, systematic investigations of the subtle interplay between the structural control of the coordination sphere and the associated metal-centered electronic properties have led to the design of monometallic lanthanide-containing devices whose *function* can be judiciously addressed and tuned.[12,15,16,21,28−31] The concomitant stimulation of lanthanide coordination chemistry by supramolecular concepts[5,41] opens new perspectives for the preparation of stable and discrete polymetallic complexes exhibiting new functions which depend on intermetallic communications.[42]

In this review, we report on the rational design of discrete polymetallic lanthanide-containing assemblies exhibiting predetermined and well-defined chemical and/or physical properties. Much attention is focused on systems for which relevant structure−function correlations are discussed together with thermodynamic properties responsible for the formation of specific assemblies in solution. This review covers the literature until October 2001, and to the best of our knowledge, only two short reviews highlighting specific synthetic[5] and magnetic[12] concepts in d−f and f−f assemblies have been previously published. Systematic descriptions of s−f,[10,11] d−f,[11,15,16] and f−f[10,15,16] aggregates are available in the literature, and this aspect will not be considered here.

II. Lanthanide Ions as Functional Centers in Elaborate Molecular Edifices

Among the plethora of applications involving lanthanide-containing edifices,[26−40] four fundamental metal-centered processes and functions can be recognized which intimately depend on the electronic structure: (1) electron transfer ability, (2) Lewis acidity, (3) optical properties (for light-emitting sensors), and (4) magnetic probes. The valence electrons of the neutral lanthanide elements Ln(0) are distributed in the 4f, 5d, and 6s orbitals, but the 4f electrons are deeply imbedded in the interior of the metal and the three valence electrons in the conduction band (two for Eu and Yb) of the metal originate preferentially from 5d and 6s orbitals.[43,44] As electrons are removed from the neutral atoms, all of these orbitals are stabilized, but the 4f are more affected than the 5d and 6s (Figure 1a). The contraction effect is so strong that even the nonvalence 5s and 5p orbitals are more expanded than the 4f shell, leading to pure [Xe]4f^n electronic configurations when three electrons have been ionized in Ln(III) (Figure 1b).[43] The extra energy required for extracting the fourth electron located in the 4f shell (I_4) is larger than the sum of the three first ionization energies, and the lanthanide ions thus exist almost exclusively as Ln(III) in molecular and supramolecular complexes.[1,3,8]

A. Redox Centers and Lewis Acids

The peculiar variations of I_3, and to a lesser extent I_4, control the accessible oxidation states of the lanthanides (Figure 2).[44] Although Ln(III) is the most common oxidation state in the complete lanthanide series, the +IV oxidation state is observed for Ce(IV) at the beginning of the series ([Xe]4f^0; $E°_{\mathrm{Ce(IV)/Ce(III)}} = +1.72$ V vs NHE) and the +II state is usually limited to Eu(II) ([Xe]4f^7; $E°_{\mathrm{Eu(III)/Eu(II)}} = -0.35$ V), Yb(II) ([Xe]4f;[14] $E°_{\mathrm{Yb(III)/Yb(II)}} = -1.05$ V), and Sm(II) ([Xe]4f^6; $E°_{\mathrm{Sm(III)/Sm(II)}} = -1.55$ V) for coordination complexes in solution.[3,8] In contrast, divalent lanthanide ions exist in the solid state for all the metals.[45] The standard reduction potentials mentioned above show that deviations from the usual Ln(III) oxidation state in solution provide strong one-electron oxidizing (Ce(IV)) or one-electron reducing agents (Eu(II), Yb(II), Sm(II)) which can work as electron-transfer devices in chemical reactions.[36,46]

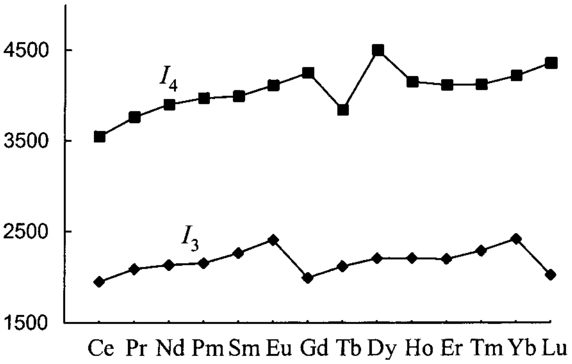
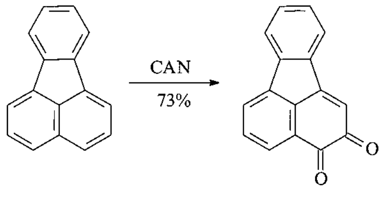
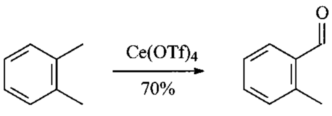


Figure 2. Variation of the third (I_3/kJ·mol^{-1}) and fourth (I_4/kJ·mol^{-1}) ionization energies along the lanthanide series.[1,44]

Ceric ammonium nitrate ((NH$_4$)$_2$Ce(NO$_3$)$_6$, CAN) and Ce(OTf)$_4$ (OTf = triflate = CF$_3$SO$_3$) are extensively used for oxidative transformations involving radical or radical cation intermediates (eqs 1 and 2).[36] Fragmentations and rearrangements of these reactive intermediates determine the nature of the isolated oxidation products, but very few detailed mechanistic studies are available for rationalizing the nature and the role of the lanthanide complexes in the oxidation process.

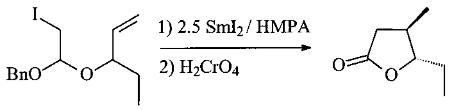


(1)

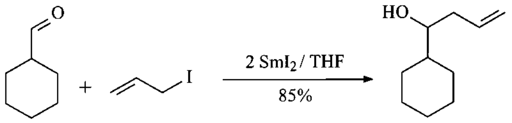


(2)

On the other hand, monometallic Ln(II) salts have been found to promote important reductive processes with exceptional tolerance for ancillary unprotected functional groups.[36,47] Samarium diiodide (SmI$_2$) has attracted much attention for one-electron reduction involving radical intermediates (eq 3) and for two-electron processes in Barbier-type reactions consuming 2 equiv of SmI$_2$ per carbonyl group (eq 4).[36a,b]

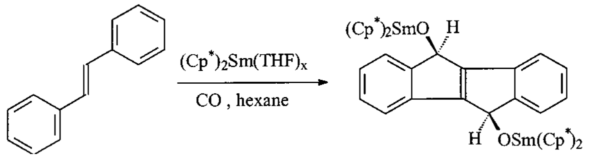


(3)



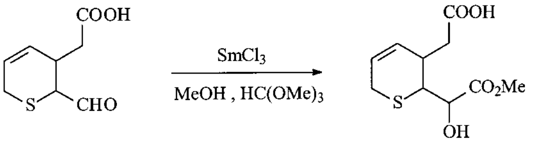
(4)

Again, very few attempts have been made to investigate the key intermediate involving the lanthanide-metal ions, but Evans and co-workers have shed some light on these transformations with the structural characterization of several metal-bonded products resulting from the reducing ability of Sm(II) in $(Cp^*)_2Sm(THF)_x$.[45,48] A striking example of the unique reductive potential of the latter complex includes the functionalization of unsaturated hydrocarbon substrates with carbon monoxide (eq 5).[49]

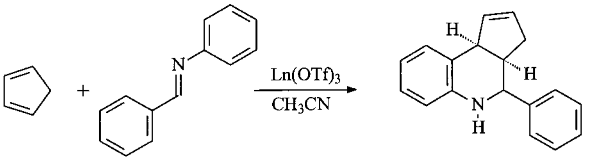


(5)

The existence of dimetallic complexes is often observed after reduction using Ln(II) or Ln metals (Ln = Sm, Yb), but no clear indication of their relevance for rationalizing chemical reactivity and mechanism has been reported[50] because unsaturated lanthanide complexes have large tendencies to dimerize or to agglomerate for producing more stable 'coordinatively saturated' assemblies.[46,51] If we now focus on the most common Ln(III) oxidation state, the poor accessibility of the 4f electrons[43] almost exclusively limits Ln−ligand bonds to electrostatic interactions between a triply charged cationic metal Ln^{3+} working as a strong oxophilic Lewis acid and Lewis base bearing partial or complete negative charges. As a result of polarization and charge reorganization occurring upon complexation of the ligands to Ln(III),[52] electrophilic groups located close to the coordinated atoms are strongly activated toward nucleophilic attacks[38] and remote acidic hydrogen atoms become more amenable to deprotonation as demonstrated by $pK_a = 7.90{-}9.01$ for the coordinated water molecules in aqueous Ln(III) (6−7 orders of magnitude more acidic than bulk water).[3] However, the larger ionic radii of Ln(III) compared to the Al(III), B(III), and Sn(IV) centers of typical Lewis acids (e.g., $AlCl_3$, BF_3, $SnCl_4$) make trivalent lanthanide ions less sensitive to hydrolysis, and they have been used as Lewis acid catalysts for organic transformations occurring in water or in hydroxylic solvents.[36,38] $LnCl_3$,[36] $Ln(OTf)_3$, and $Ln(ClO_4)_3$[38] are particularly efficient as catalysts for C−C bond formation resulting from activation of aldehydes (eq 6) and Diels−Alder reactions (eq 7).

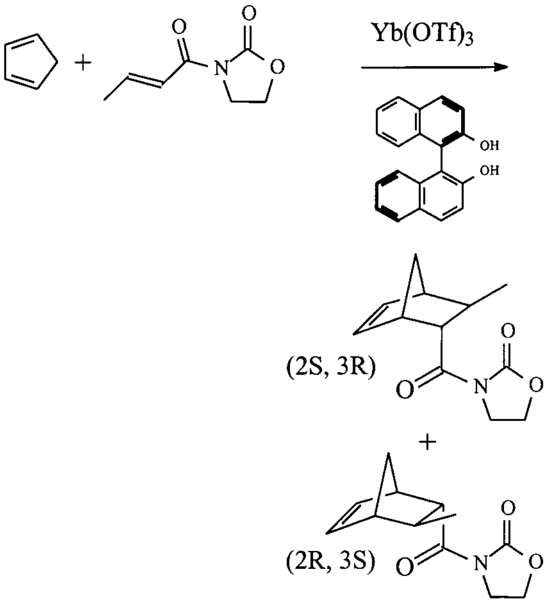


(6)



(7)

Systematic studies along the lanthanide series generally point to better yields with smaller Ln(III) ions because of their increased acidities.[38] Asymmetric versions of these organic transformations can be obtained with more sophisticated Ln(III) catalysts in which the metal is coordinated by chiral binaphtholate ligands (eq 8). Excellent enantiomeric excesses have been reported (ee = 60−93%) for these and related reactions, but ee strongly depends on the specific coordination numbers of Yb(III) in the active catalyst.



(8)

During the hydrolytic cleavage of DNA phosphate by enzymes containing metal centers, both the electrophilic and the nucleophilic centers can be activated by coordination to Ln(III) because the metal ion promotes hydrolysis by (i) neutralization of the initial negative phosphate charge as well as the developing charge in the pentavalent phosphorus intermediate, (ii) stabilization of the transition state, (iii) lowering the pK_a of the bound water (or alcohol) molecule, and (iv) stabilization of the leaving group bearing the phosphate (Figure 3).[53]

Monometallic Ln(III) complexes have been known for several decades to work as Lewis acid catalysts for hydrolyzing phosphodiesters,[54] but significantly larger efficiencies have been reported for dimetallic[55−57] and polymetallic[58] lanthanide-containing assemblies since the different steps of the activation process can be promoted by more specific and adapted catalytic sites. It is thought that deprotonation of water for providing the active hydroxide nucleophile is the primordial step, and the low pK_a of water molecules bridging two Ln(III) in polymetallic complexes is a noticeable advantage.[56] Moreover, the simultaneous electrostatic stabilization of the bound phosphate

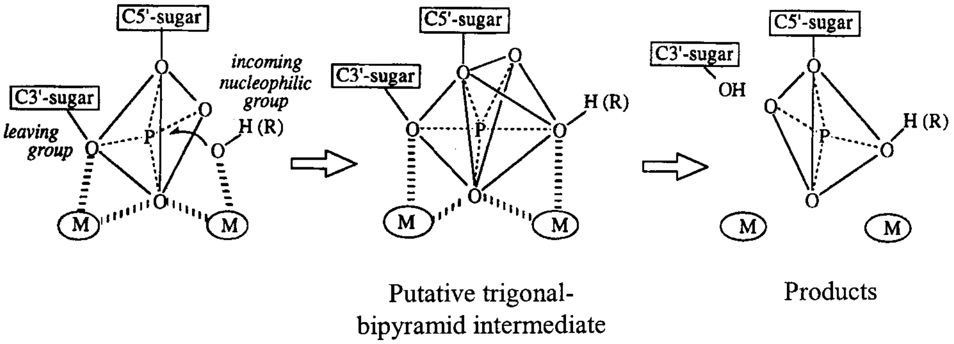


Figure 3. Schematic proposed DNA phosphate hydrolysis by enzymes containing dimetallic metal centers. Solid lines indicate the geometry around the central phosphorus atom. (Reprinted with permission from ref 53. Copyright 1998 Academic Press.)

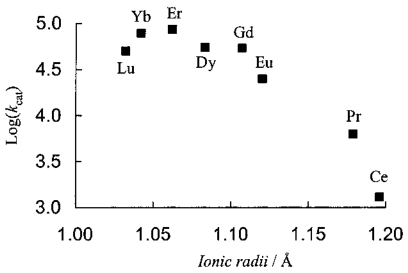


Figure 4. Dependence of the bis(nitrophenyl)phosphate hydrolysis rate constants, $k_{cat} \times 10^4$ (s^{-1}), on the ionic radii (Å) of nine-coordinate lanthanide ions.[59]

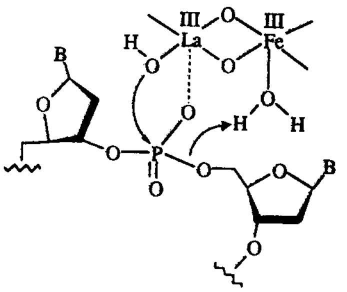


Figure 5. Proposed mechanism of DNA or RNA hydrolysis mediated by La(III)/Fe(III). (Reprinted with permission from ref 53. Copyright 1998 Academic Press.)

group at one end of the complex and activation of water at the other end requires a structurally well-defined dimetallic center.[54−58] Interestingly, Schneider and co-workers demonstrated that (i) all aqueous Ln^{3+} display Michaelis−Menten saturation kinetics for the hydrolysis of the model compound bis(nitrophenyl)phosphate (pH = 7, 50 °C) and (ii) a strict correlation with the ionic radii of the cations is evidenced (Figure 4).[59] The improved efficiency of the catalytic pathway observed for smaller Ln(III) is obviously ascribed to the larger Lewis acidity of the cation which enhances both water deprotonation and phosphoryl activation. The unexpected decrease of k_{cat} for the heaviest Ln(III) (Ln = Yb, Lu) contrasts with this trend and can be traced back to clustering and aggregation which remove free coordination sites for metallic activation of substrates.

The design of an efficient lanthanide-containing catalyst thus requires a precise structural, topological, and electronic control of the metallic sites within the polymetallic assembly. Homodi- to polymetallic lanthanide complexes offer similar metallic sites which are difficult to optimize separately for a specific task. Although scrambling processes strongly limit the preparation of pure labile heterodimetallic complexes, the association of Ln(III) with kinetically inert Fe(III) efficiently promotes the hydrolysis of RNA and DNA simplified substrates (Figure 5).[60] One metal of the pair binds a water molecule with a moderate pK_a value compatible with a strong nucleophilic activity after deprotonation (lanthanide site, p$K_a \approx$ 7.5−8.5),[3] and the other metal is a stronger Lewis acid for stabilizing the hydroxylic leaving group (Fe(III) site).[61] Such association is not limited to the specific hydrolysis of phosphodiester, and related heterodimetallic s−f complexes have been successfully used for promoting Lewis-acid-catalyzed asymmetric reactions including the stereoselective formation of C−C, C−O, and C−P bonds.[39,62]

B. Optical, Spectroscopic, and Magnetic Probes

Beyond the tunable redox and Lewis acid functions associated with the peculiar [Xe]4f^n electronic configurations of Ln(III) in complexes, the existence of low-energy excited states resulting from internal 4f → 4f electronic transitions induces fascinating metal-centered spectroscopic properties. The lack of significant participation of 4f electrons to chemical bonding provides line-like 4f → 4f absorption and emission bands with negligible Stokes shifts and excessively low probabilities of transitions ($\epsilon \leq 1$ $M^{-1} \cdot cm^{-1}$) because 4f → 4f transitions are parity-forbidden (Laporte's rule) and because most of the transitions are also forbidden by the spin selection rule.[63,64] The energies and splitting patterns of the ground and excited states can be rationalized via the Russell−Saunders approach which considers $J = L + S$ being a satisfying quantum number, specific crystal-field effects being further applied as perturbation of the original spin−orbit spectroscopic terms.[25,43] It becomes thus possible to reliably predict and control the energy levels of the spectroscopic terms (and the associated optical and spectroscopic properties) within elaborated lanthanide assemblies possessing well-defined metallic sites. The low probabilities associated with the 4f → 4f transitions severely limit the use of Ln(III) as optical sensors since high input power is required to obtain traceable signals, but the associated excited lifetimes extend into the micro- to millisecond domains, a crucial advantage for the design of luminescent materials

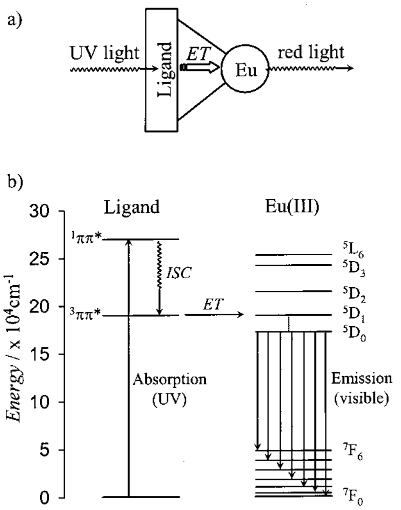


Figure 6. (a) Schematic representation of the *antenna* effect occurring in monometallic Eu(III) complexes possessing aromatic light-harvesting chromophores and (b) associated energy level diagram (*ISC* = intersystem crossing, *ET* = energy transfer).

with practical applications.[31,63,64] Considering that the metal-centered excited states can be efficiently fed by energy transfer processes involving peripheral light-harvesting chromophores (antenna effect),[65] the long-lived line-like metal-centered visible or near-infrared emissions of Nd(III), Eu(III), Tb(III), and Yb(III) have been extensively used as a luminescent flag[32,66] for (i) labeling biological materials,[30,31,67,68] (ii) sensing nonchiral[29,69] and chiral[71] analytes, and (iii) probing metallic environments because the specific splitting pattern of the emission bands can be explained in term of the microsymmetry of the crystal field (Figure 6).[63] An other important practical consequence of the sharp and forbidden 4f → 4f transitions concerns the production of sufficient radiant power per bandwidth compatible with stimulated emission and LASER functions.[64] The growing need for efficient lasers at wavelengths in the near-infrared for information transfer in optical fibers (NIR lasers) has recently motivated new developments of Nd(III), Er(III), and Tm(III) garnets.[23,71]

Generally speaking, the design of a luminescent lanthanide sensor or probe requires a unique combination of features: (i) protection of the included lanthanide ions from quenching by high-energy vibrations (solvent molecules or ligating groups), (ii) multiple absorbing groups suitable for light-harvesting and energy transfer in order to efficiently feed the metal-centered excited states, (iii) high thermodynamic stability and kinetic inertness, and (iv) specified solubility and nontoxicity if these sensors are to be used in biological media.[72,73] Only an elaborated metallic coordination sphere may simultaneously fulfill these criteria, but the inherent flexibility and lability of lanthanide assemblies severely limit the preparation of discrete complexes in solution, and long-range order provided by packing forces in the solid state has been used to overcome these limitations.[23,64,74] However, some recent advances in controlling the lanthanide coordination sphere with preorganized macrocyclic ligands or predetermined acyclic chelating receptors (vide supra) demonstrate that programmed discrete assemblies working as luminescent sensors in solution are accessible.[67–77] Moreover, optical properties can be significantly improved if the lanthanide-centered luminescent properties can be rationally triggered by specific quenching processes involving electron[75] or energy transfers[76] in polymetallic edifices. Pioneer work in this field can be traced back to (i) K^+-controlled photoinduced electron transfer (PET) quenching of Eu(III) luminescence in terpyridine chelates bearing azacrown ethers (s−f system, Figure 7a),[75] (ii) tunable intramolecular Eu(III) → Fe(II) energy transfers in heterodimetallic triple-stranded helicates (d−f system, Figure 7b),[42] and (iii) intramolecular Tb(III) → Eu(III) energy transfers in statistically doped solid-state materials (f−f systems).[24,76]

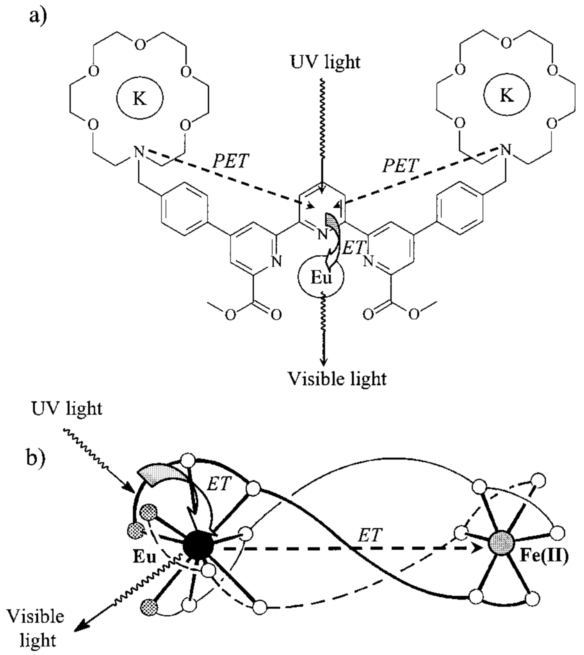


Figure 7. (a) Trigerring of lanthanide-centered luminescence in a polymetallic s−f complex (*PET* = photoinduced electron transfer). The fixation of K^+ removes PET involving the lone pair of the nitrogen atom and luminescence occurs.[75] (b) Trigerring of lanthanide-centered luminescence in a polymetallic d−f complex (*ET* = photoinduced electron transfer). The change in the Fe(II) spin state dramatically affects the intramolecular energy transfer process.[42]

Finally, peculiar metal-centered magnetic properties result from the $[Xe]4f^n$ electronic configurations of Ln(III) which can be exploited to design functional devices. The existence of seven 4f orbitals provides metals and/or ions with a large number of unpaired electrons and considerable associated electronic magnetic moments for midrange lanthanides (Ln = Gd−Er).[1,8] Although orbital contributions to the electronic spin moment produce the highest magnetic moments for the $[Xe]4f^{8-11}$ configurations, specific functions are enhanced by the peculiar symmetric electronic ground state ^8S of Gd(III) ($[Xe]4f^7$). For instance, its unique long electronic relaxation time opens fascinating perspectives for enhancing nuclear relaxation of peripheral atoms via contact, dipolar, or spin-Curie interactions.[77,78] The recent development of MRI (magnetic resonance imaging) contrast agents takes

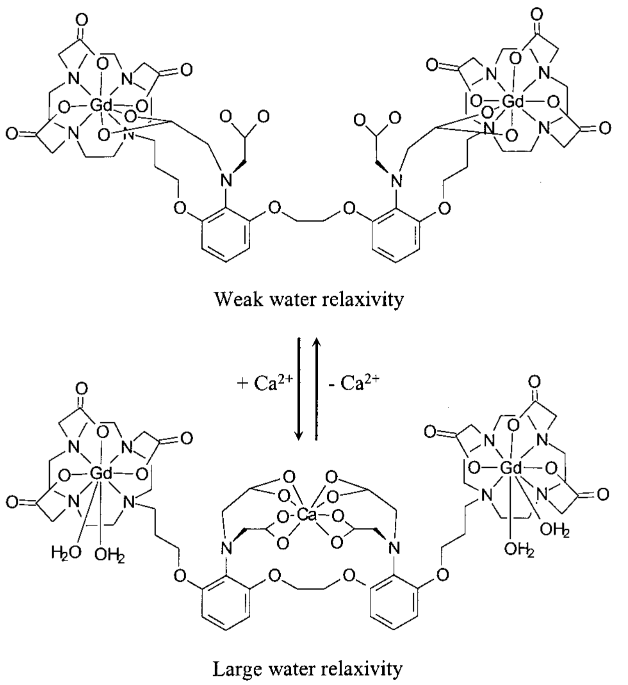


Figure 8. Schematic representation of a Ca(II)-sensitive MRI contrast agent.[81]

advantage of the strong dipolar coupling between the electronic magnetic moment of Gd(III) and the nuclear magnetic moment of water molecules entering the first coordination sphere of the lanthanide complex in order to enhance relaxivity of the solvent close to the paramagnetic probe.[28,79] Since solvent relaxivity depends on the number of accessible metallic sites for water molecules, changes in the coordination sphere induced by external stimuli, such as hydrolysis of the blocking group in galactopyranose-derivatized [Gd(DOTA)] (DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate)[80] or decomplexation of the pendant arms by competition with Ca^{2+} [81] or H^+,[82] can be used to trigger the contrast effect of the Gd complexes (Figure 8). A new generation of 'smart' and noninvasive MRI contrast agents sensitive to external stimuli (pH, pO_2, intracellular concentrations of specific analytes) is currently the subject of intense research.[79]

For lanthanides possessing large orbital contributions (i.e., Ln = Tb–Yb), the weak crystal-field splitting induced by the coordinated ligands is sufficient to produce magnetic anisotropies 1 or 2 orders of magnitude larger than those obtained for diamagnetic materials.[33] Lanthanide-containing liquid crystals or matrices are thus used for their capability to align proteins in magnetic fields and to give access to residual dipolar N–H couplings, a crucial point for conformational studies of biological materials in solution.[83] Moreover, large magnetic anisotropies induce through-space paramagnetic hyperfine NMR shifts (i.e., pseudo-contact shifts), which were originally used for assigning structures of complicated organic molecules at low magnetic fields (shift reagents).[84] Theoretical advances in the 1970s proposed a satisfying modeling of the pseudo-contact shift (eq 9, C_j and D_j are magnetic constants characteristic of the lanthanide j and $A_2^0\langle r^2\rangle$ and $A_2^2\langle r^2\rangle$ are the second-rank crystal-field parameters),[85] and 3D molecular structures of lanthanide complexes became accessible via the determination of the internal polar coordinates of NMR-active nuclei (Figure 9).[86]

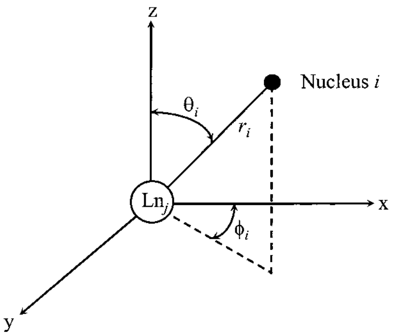


Figure 9. Definition of the internal polar coordinates of a nucleus i in the complex of a lanthanide j (x, y, z are the principal axes of the magnetic susceptibility tensor).

$$\delta_{ij}^{\text{pseudo-contact}} = \frac{1}{T^2}\cdot\left[A_2^0\langle r^2\rangle\cdot C_j\cdot\left(\frac{3\cos^2(\theta_i) - 1}{r_i^3}\right) + A_2^2\langle r^2\rangle\cdot\left(\frac{\sin^2(\theta_i)\cdot\cos(2\phi_i)}{r_i^3}\right)\right] \quad (9)$$

Since spin delocalization according to the Fermi mechanism (i.e., contact contribution) is limited to atoms close to the metallic center and does not affect peripheral nuclei, pure pseudo-contact contributions can be easily measured and used for extracting 3D structures, not only for low-molecular weight lanthanide complexes,[86] but also for large proteins where Ca(II) has been replaced by Ln(III).[87] Further modeling of the contact contribution[88] allows the reliable separation of contact and pseudo-contact contributions, which opens new perspectives for (i) improving the structural characterization of supramolecular lanthanide complexes in solution[89] and (ii) designing paramagnetic probes monitoring temperature in biological media.[90] Lanthanide-containing polymetallic complexes have been prepared for increasing the density of paramagnetic relaxation probes in the same MRI contrast agent (Figure 10a,b).[91,92] Detailed studies point to electronic dipolar coupling in Gd–Gd pairs which increases electronic relaxation and consequently limits relaxivity. Nanometric spherical and rigid particles obtained by self-aggregation of a gadolinium podate (Figure 10c) through intermolecular weak bonds have also been tested and display an unusually large relaxivity while retaining an encouraging stability in dilute solution.[93] On the other hand, paramagnetic structural probes based on pseudo-contact contributions can benefit from the presence of two paramagnetic metal ions in the same assembly to improve sensitivity to minor structural distortions (Figure 10d).[89] Although fascinating advantages could result from the triggering of electron-spin relaxation in magnetically coupled dimers,[94] the weak to negligible magnetic coupling evidenced in polymetallic d–f and f–f complexes[15–22] has prevented applications in this field.

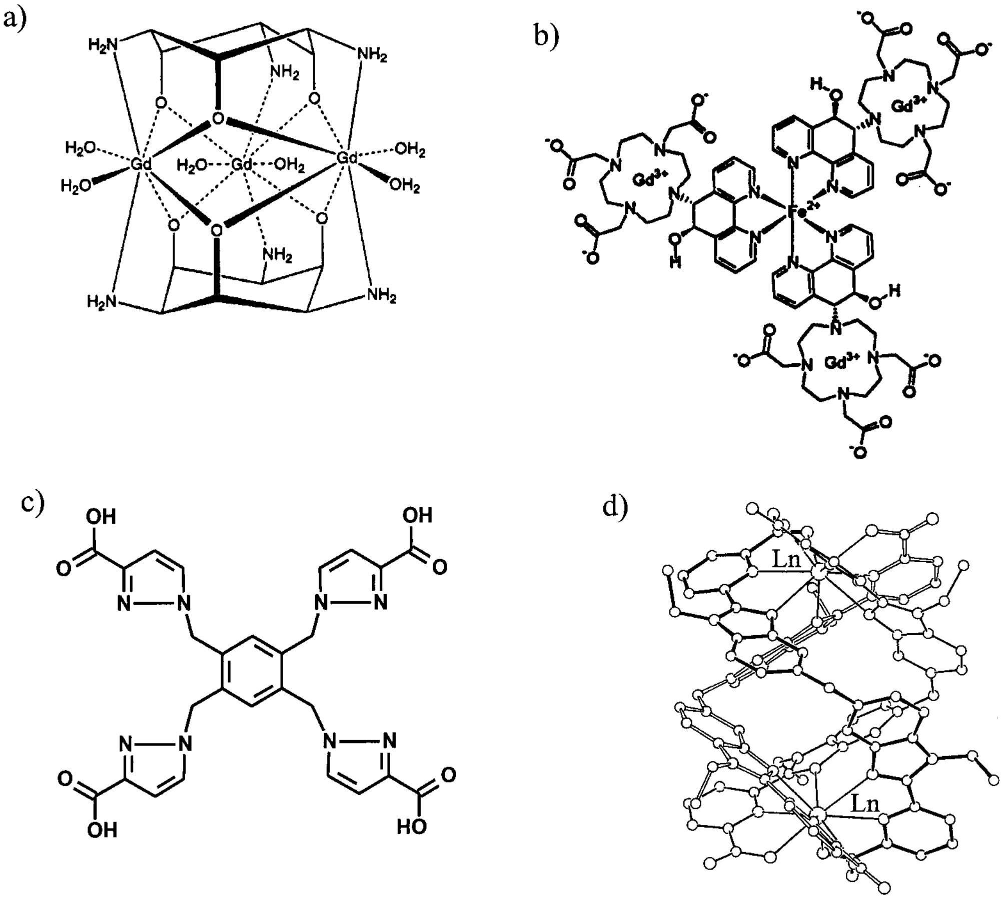


Figure 10. Selected polymetallic f−f and d−f edifices: (a[91], b[92], and c[93]) polymetallic MRI contrast agents and (d) highly sensitive paramagnetic dimetallic f−f structural probe.[89b]

This brief survey of functional complexes in which the lanthanide-metal ions act as redox, acid, luminescent, or magnetically active centers demonstrates that their intrinsic 'free-ion' electronic properties represent the main motivation for their introduction into discrete assemblies and sophisticated materials. However, further fine-tuning of these properties required for specific applications and functions relies on a precise control of the metallic environment which controls polarization, accessibility of the metal ion, and crystal-field splitting of the electronic levels.

III. Synthesis of Elaborated Lanthanide-Containing Edifices

Since spherical trivalent lanthanides are among the most labile[95] and stereochemically versatile[1,3] metal ions, a close and rational control of the metallic coordination sphere entirely relies on conformational restriction of the receptors and/or interligand interactions. Except for some macrocyclic platforms bearing ionizable pendant arms (e.g., carboxylates or phosphonates grafted on cyclen or calix[*n*]arene frameworks),[96] octadentate polyaminocarboxylates,[96] and double- or triple-decker sandwiches with phthalocyanin or pophyrins[37] which give inert lanthanide complexes in solution, a kinetic resolution of lanthanide complexes on the synthetic scale remains largely inaccessible and only fast-measurement techniques (fluorescence, X-ray diffraction) reflect fixed and well-defined geometries and arrangements in solution. The selective introduction of Ln(III) into organized molecular edifices thus relies on thermodynamic control of the complexation process in which well-defined (usually labile) species are produced in solution which can be then isolated by crystallization.[5] Detailed thermodynamic investigations of lanthanide complexation processes in water point to a remarkable compensation effect responsible for the emergence of the well-known electrostatic trend, i.e., a monotonic increase of the formation constants of the complexes with the decreasing size of $\mathrm{Ln^{III}}$.[8,97] Two successive steps can be written for the net complexation reaction of a $\mathrm{Ln^{III}}$ ion with a ligand L corresponding to dehydration (eq 10) followed by the combination of the desolvated partners (eq 11).

$$[\mathrm{Ln(H_2O)}_n]^{3+} + [\mathrm{L(H_2O)}_p]^{x-} \rightleftharpoons [\mathrm{Ln(H_2O)}_m]^{3+} + [\mathrm{L(H_2O)}_q]^{x-} + (n - m + p - q)\ \mathrm{H_2O} \qquad (10)$$

$$[\mathrm{Ln(H_2O)}_m]^{3+} + [\mathrm{L(H_2O)}_q]^{x-} \rightleftharpoons [\mathrm{LnL(H_2O)}_{m+q}]^{(3-x)+} \qquad (11)$$

Opposite enthalpic and entropic contributions are expected for each reaction, but the compensation effect assumes that the free energy for the dehydration process (eq 10) is negligible at room temperature because $\Delta H_{10} \approx T\Delta S_{10}$. The global free energy of the complexation process is thus dominated by the enthalpy-driven combination step ($\Delta G_{\text{global}} = \Delta G_{10} + \Delta G_{11} \approx \Delta G_{11}$), leading to increased formation constants with increasing charge density on the cation. Although this simple approach is often used as a guideline for interpreting thermodynamic data for lanthanide complexes, the introduction of steric constraints, preorganization, and/or chelate effects within sophisticated receptors may alter the expected electrostatic trend because specific intramolecular interactions and solvation effects are not considered in this simple model. Some minor selectivity (=deviation from the electrostatic trend) for the complexation of Ln^{III} has been evidenced for polycarboxylates and related acyclic polydentate receptors, but the rationalization of these observations is difficult and the associated structural control is limited. While classical chelate effects in lanthanide complexes favor complexation by increasing ΔS_{10} (gain in translational entropy associated with the larger desolvation of the metal required for coordination of the chelate),[98] equilibrium 11 is poorly affected and selectivity is not significantly improved.[97] In fact, ΔH_{11} and ΔS_{11} depend on the intimate interactions occurring between the receptor (host) and the desolvated metal ion (guest) and can be modulated by using the lock-and-key[99] and the induced fit[100] concepts. Equations 10 and 11 are sufficiently general to rationalize the thermodynamics of lanthanide complexes in nonaqueous solvents (i.e., H_2O replaced by solvent molecules), but the reduced solvation observed in less polar solvents decreases ΔH_{10} and favors lanthanide complexation. Enthalpy-driven complexation processes with ligands displaying limited affinities for Ln(III) (ΔH_{11} is only slightly negative) can be then envisioned, and lanthanide complexes with tetrahydrofuran, cyclopentadienyl anion,[10,11] and heterocyclic nitrogen donors[6] are accessible in organic solvents.

A. Lock-and-Key Principle in Monometallic Lanthanide Complexes

An efficient preorganization of the donor sites in the receptors combined with a strict steric match between the cavity of the host and the ionic size of the Ln(III) guest limit the electrostatic work required for optimizing the dative bonds formed in the complexes and maximize the enthalpic contribution to the complexation process (ΔH_{11}).[97,98] Although preorganization also provides some favorable contributions to ΔS_{11} (i.e., ΔS_{11} becomes less negative because of the minimal loss of conformational and vibrational entropies),[101] the dominant translational entropic term (ΔS_{10}) is not affected and enthalpic stabilization represents the basis of the lock-and-key concept.[99] Following the initial work on alkaline and alkaline-earth cations,[102] macrocyclic crown ethers with controllable cavities have been chosen to test size-discriminating effects along the lanthanide series.[103] Although a macrocyclic effect is expected to induce selectivity for crown ethers possessing the best adjusted cavity, the observed size-discriminating effect in $[Ln(L)]^{3+}$ complexes is small ($\Delta\log(K) = 1-2$). The expected trend is however respected with 18-crown-6 favoring complexes with the large La(III) and 15-crown-5 more efficiently coordinating the small Lu(III) (Figure 11). This deceiving behavior can be ascribed to (i) the limited rigidity of the macrocycles which can adapt their conformation to smaller metal ions[98] and (ii) the lack of fine-tuning of the cavity size since the introduction of a $(CH_2)_2-O$ unit enlarges the cavity by 0.5−0.7 Å, a difference 2−3 times larger than the contraction of Ln(III) along the complete lanthanide series!

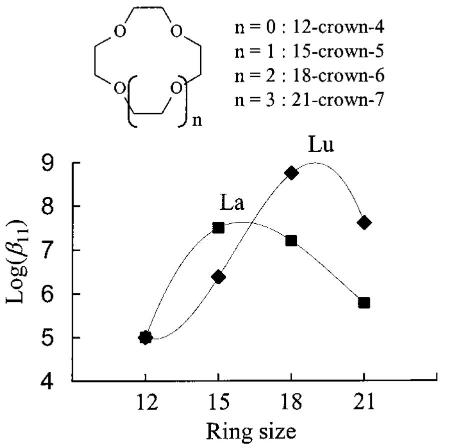


Figure 11. Size-discriminating effect in Ln(III) 1:1 complexes with crown ethers (■) $[LaL]^{3+}$and (◆) $[LuL]^{3+}$ in anhydrous propylene carbonate.[103b] The trend lines are only guides for the eyes. Units for $\beta_{11} = M^{-1}$.

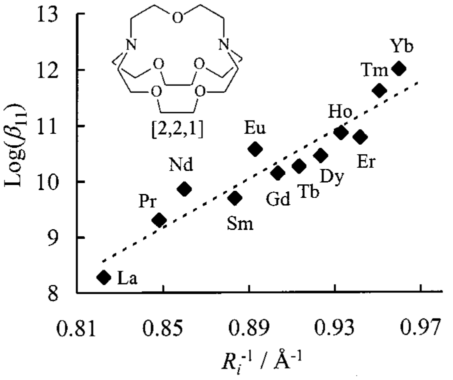
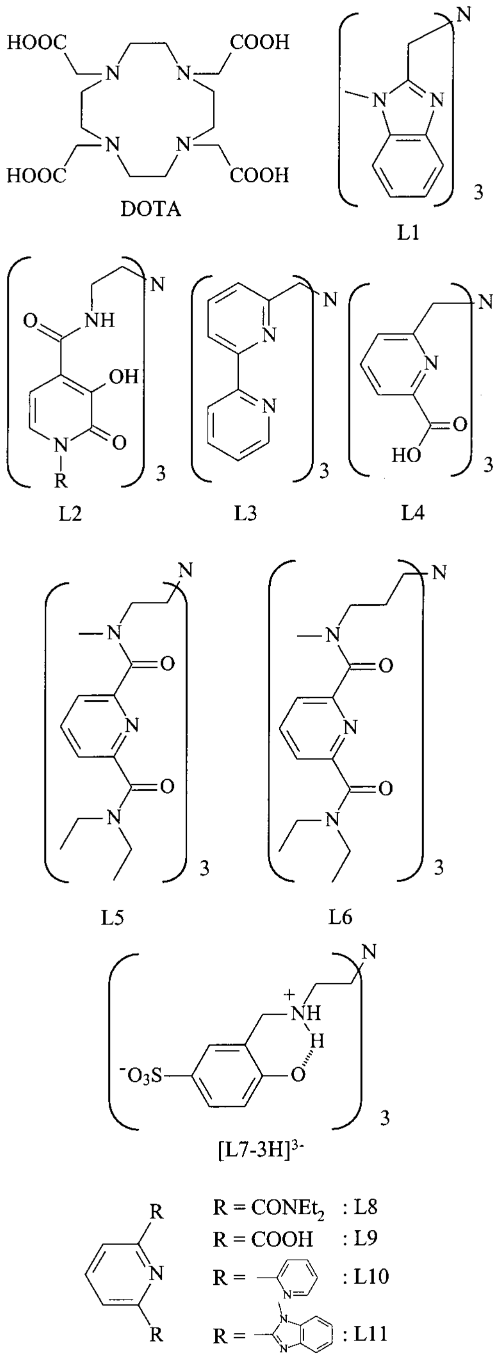


Figure 12. Formation constants of the cryptates $[Ln-[2,2,1])]^{3+}$ in methanol in functions of the inverse of nine-coordinate lanthanide ionic radii.[104] Units for $\beta_{11} = M^{-1}$.

Moving to more rigid macrobicyclic receptors (cryptands) does not significantly improve the situation since ultra-fine-tuning of the cavity is even more difficult for sterically constrained systems and classical electrostatic trends are generally obtained (Figure 12).[103,104] To circumvent some of the limitations encountered with rigid monocyclic and dicyclic receptors, ionizable macrocycles have been developed, bearing pendant arms fitted most frequently with carboxylic or phosphorus-containing acid functions.[92,96,105] The presence of the latter leads to the formation of strong complexes, owing to hard ion−ion interaction between Ln(III) and the carboxylate anions. The ligands are intermediate between preorganized (lock-and-key principle) and predisposed (induced fit principle) entities, since the complexed pendant arms usually have a different conformation than that observed in the free ligand and they can adapt to the varying size of the Ln(III) ions. Several platforms have been used to graft these arms: crown ethers, diazapolyoxocycloalkanes, cyclen and other polyazacycloalkanes, and more recently calixarenes. Although significant size-selective effects are usually not observed within the Ln(III) series, these ionizable macrocycles proved to be good chelating agents for the selective complexation of lanthanides over alkali and alkaline-earth cations.[106] A general trend is that the stability can be slightly tuned by adjusting the ring size and the number of donor atoms of the platform as well as the number of arms to form a suitable cage structure for the Ln(III) ion. Among all the ligands tested, DOTA proved to be one of the best sequestering agents for Ln(III) ions, with log K in the range 22−26, but the flexible pendant arms easily adapt the cavity for the entering Ln(III), and a classical electrostatic trend is observed along the lanthanide series (i.e., the stability of the complexes increases with increasing charge density on the metal), Chart 1.

Reducing the macrocyclic platform to a single atom provides tetradentate (L1),[107] hexadentate (L2),[108] heptadentate (L3, L4),[109] and nonadentate (L5, L6)[110] tripodal podand-type ligands partially preorganized for the complexation of Ln(III). Thermodynamic studies demonstrate that negatively charged oxygen donors in L2[108] and L4[109] are crucial for producing Ln−ligand bonds strong enough to survive competition with water molecules ($\Delta H_{11} > -\Delta H_{10}$). Moreover, the favorable entropic contribution of the podand effect (i.e., a special case of chelate effect)[98] allows the synthesis of stable complexes [Ln(L2−3H)(H_2O)$_2$] and [Ln(L4−3H)(H_2O)$_2$] in which two vacant coordination positions are occupied by water molecules, an encouraging point for the design of new MRI contrast agents with improved efficiencies.[108,109] However, the increased flexibility of the podand compared to bicyclic and monocyclic receptors limits the enthalpic contribution of preorganization to ΔH_{11}, and this has deleterious effects on both stability and selectivity. The considerable decrease of the formation constants (1−2 orders of magnitude) observed when going from rigid ethyl spacers in nine-coordinate podates [Ln(L5)]$^{3+}$ to more flexible propyl spacers in [Ln(L6)]$^{3+}$ confirms this trend[110] and strongly suggests that compensation effects are necessary to restore large formation constants and selectivity along the lanthanide series. According to this reasoning, Orvig and co-workers[111] used an intramolecular network of noncovalent NH···O hydrogen bonds to predispose the zwitterionic podand [L7−3H]$^{3-}$ for its complexation to Ln(III). The larger enthalpic contribution to ΔH_{11} provides water-stable [Ln(L7−3H)(H_2O)$_6$] and [Ln(L7−3H)$_2$(H_2O)]$^{3-}$ complexes which exhibit an unprecedented selectivity for small Ln(III) ($\Delta\log(\beta_2) = \log(\beta_2^{\mathrm{Lu}}) - \log(\beta_2^{\mathrm{La}}) = 5.5$) tentatively assigned to a favorable tightening of the hydrogen bonds with small Ln(III). Hydrogen bonds[110,111] represent only a specific case of compensation effects, and other secondary noncovalent interactions such as van der Waals[111,112] and electrostatic interactions[113] can be judiciously implemented to increase ΔH_{11} and ΔS_{11} (i.e., ΔS_{11} becomes less negative).[114]

Chart 1



B. Induced Fit Principle in Monometallic Lanthanide Complexes

This principle has deep roots in biological processes in which the loss of conformational entropy associated with protein−ligand binding is more than offset by favorable enthalpic contributions originating from secondary noncovalent interactions.[101,115] Specific orientations of the interacting ligands result from the optimization of these interactions which control the stability and the geometry of the host−guest complex: a crucial point if this approach is foreseen for the design of functional lanthanide complexes. The unambiguous application of this concept to Ln(III) has slowly emerged during the past decade with the rational preparation of triple-helical nine-coordinate

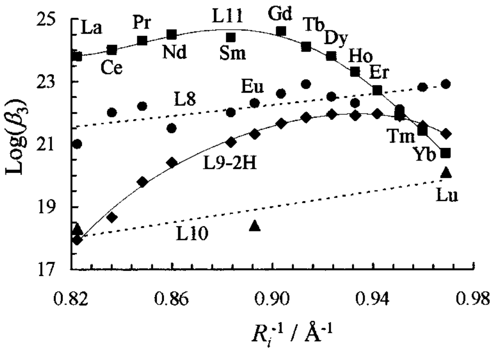


Figure 13. Cumulative formation constants log(β_3) of [Ln(L8)$_3$]$^{3+}$ (●),[116] [Ln(L10)$_3$]$^{3+}$ (▲),[117b] and [Ln(L11)$_3$]$^{3+}$ (■)[112] in acetonitrile (298 K) and [Ln(L9−2H)$_3$]$^{3-}$ (♦)[113] in water (298 K) versus the inverse of the ionic radii of nine-coordinate Ln^{III}. Units for β_3 = M^{-3}.

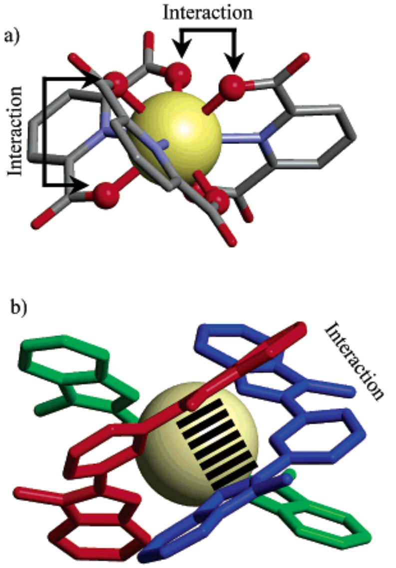


Figure 14. Schematic representation of secondary noncovalent interstrand interactions in (a) [Ln(L9−2H)$_3$]$^{3-}$ (charge−charge) and (b) [Ln(L11)$_3$]$^{3+}$ (π-stacking).

complexes in which semirigid tridentate chelating units programmed for producing noncovalent interactions are wrapped around and bound to a central Ln(III). The pseudo-D_3-symmetrical complexes [Ln(L8)$_3$]$^{3+}$ [116] and [Ln(L10)$_3$]$^{3+}$ [117] do not exhibit significant noncovalent interstrand interactions, and eqs 10 and 11 hold for rationalizing their thermodynamic behavior which is characterized by classical electrostatic trends in acetonitrile (Figure 13). The hydrolysis of the terminal amide groups of L8 produces the well-known dipicolinate dianion [L9−2H]$^{2-}$ which gives stable triple-helical complexes [Ln(L9−2H)$_3$]$^{3-}$ in water.[113] Although fast oscillations of the pyridine rings on the NMR time scale induce distortions from regular triple-helical structures for large Ln(III) in solution,[118] the deviation from the expected electrostatic trend (Figure 13) can be traced back to secondary electrostatic (charge−charge) repulsions between coordinated carboxylate groups which are brought closer by coordination to small Ln(III) (Figure 14a).[5,113] On the other hand, extension of the aromatic side-arms in L11 increases the length of the wrapped threads in [Ln(L11)$_3$]$^{3+}$ and allows efficient intramolecular interstrand π-stacking interactions (Figure 14b). Optimal stabilization is observed for midrange Ln(III), and the abrupt decrease of the formation constants for small Ln(III) reflects strong repulsive van der Waals interstrand interactions (Figure 13).[112] These examples illustrate how a judicious programming of secondary noncovalent interactions expressed in the final complexes contributes to the selective introduction of Ln(III) into elaborated edifices.

C. Planning Discrete Lanthanide-Containing Polymetallic Assemblies

Considering the difficulties inherent in the preparation of organized monometallic lanthanide complexes, it is not surprising that the selective incorporation of Ln(III) into polymetallic edifices remains a fascinating challenge in metallosupramolecular chemistry. Irrespective of the selected strategy (lock-and-key or induced fit), extension toward polymetallic is accompanied by a significant increase in the number of coordination sites to program into the receptors. Homopolymetallic assemblies usually result from the introduction of sets of identical or similar coordination sites, whereas the selective recognition of different metal ions requires a more sophisticated coding of the different segments for one particular metal.

Preorganization offers straightforward perspectives since two or more rigid (branched) macrocyclic mono- or bicyclic receptors can be connected by adapted spacers. The polymetallic Gd(III) complexes working as MRI contrast agents studied by Merbach and co-workers[119,120] as well as those recently developed by Desreux and co-workers (Figure 10b)[92] and by Meade and co-workers (Figure 8)[81] follow this strategy, the kinetic inertness of the [Gd(dota-R)] units preventing scrambling between the different metal ions. Potential hosts made of two or more macrocycles held at a suitable distance by rigid and inert spacers is a logical extension of this approach, but the difficult fine-tuning of each compartment for the specific recognition of one particular Ln(III) has discouraged pioneer work along this line. An alternative strategy uses large macrocycles in which two or more metal ions interact with specific and preorganized binding segments. The isolation of homodimetallic f−f complexes, [Gd$_2$(L12−6H)(H$_2$O)$_2$],[121] [Eu$_2$(L13b-6H)(DMF)$_5$],[122] [Ln$_2$(L14−2H)(NO$_3$)$_4$],[123] [Ln$_2$(L15−2H)(NO$_3$)$_4$],[124] and [La$_2$(L16−2H)(OAc)$_4$],[125] represents undeniable successes in which the nature of the coordination sites and the intermetallic separations (which range from 3.81 Å in [Eu$_2$(L13b-6H)(DMF)$_5$] to 10.89 Å in [Gd$_2$(L12−6H)(H$_2$O)$_2$]) can be roughly programmed. For the Schiff base derivatives L14-L16, Ln(III) are generally used as template agents and heterodimetallic versions of these reactions have been attempted to produce less symmetrical macrocyclic receptors such as L17, which is obtained as its heterodimetallic complex [LnNi(L17−2H)]$^{3+}$, Chart 2.[126]

Recently, more rigid macrobicyclic dimetallic f−f complexes [Ln$_2$(L18−3H)(NO$_3$)$_2$]$^{3+}$ (Ln = Dy, Lu) have been prepared,[127] but no thermodynamic data are available to support possible enthalpic (and/or entropic) macrobicyclic effect.[98] Since the number of

Chart 2

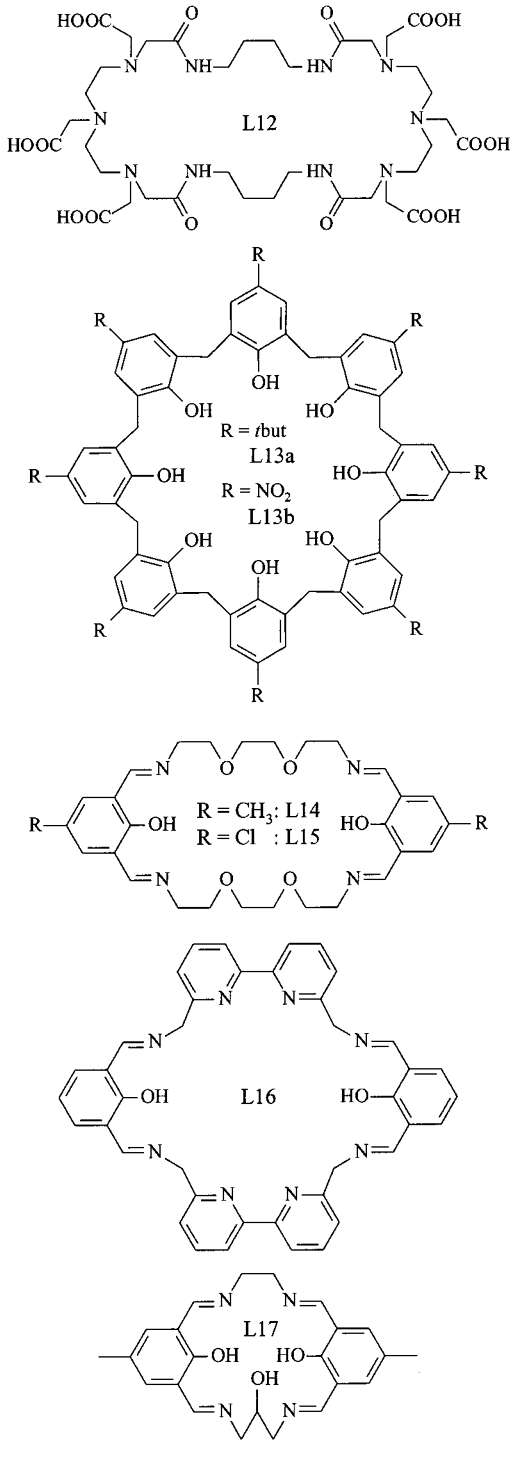
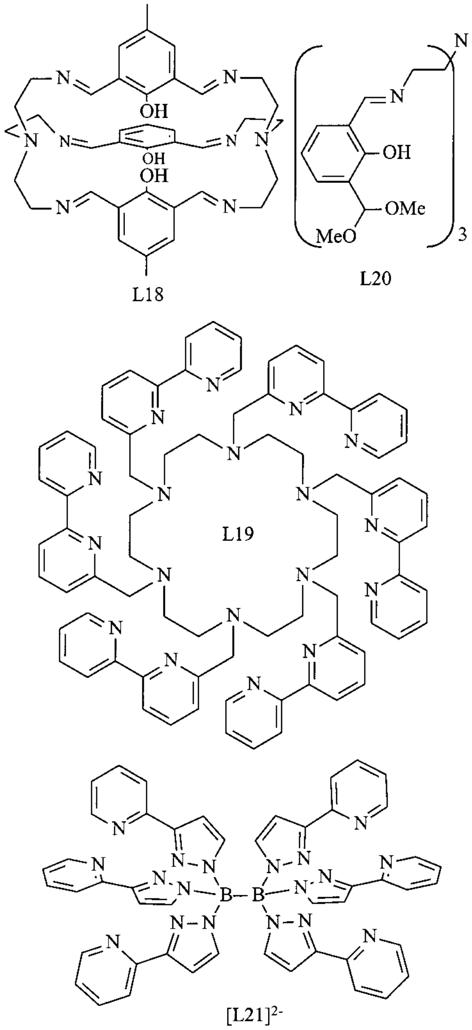


Chart 3



donor atoms drastically increases for polymetallic edifices, mono- (L12)[121] and bidentate (L19)[128] appended sidearms have been grafted onto the macrocyclic platform to favor efficient complexation of two or more metal ions (Chart 3).

As described previously for monometallic complexes, reducing the platform to a single atom produces podands, but the limited number of available donor atoms is rarely compatible with the formation of discrete polymetallic edifices. Some interesting exceptions result from a special design of the receptors. For instance, the terminal acetal groups of L20 provide six closely spaced donor sites in $[LaNi(L20-3H)(OH_2)]^{2+}$ which are coordinated to La(III) whose nonadentate coordination sphere is completed by three deprotonated phenolate oxygen atoms. The noncoordinated imines of the tripodal spacers can be used for further complexation, and a pseudo-octahedral Ni(II) cation can fit into the cavity defined by the imines and the oxygen atoms of the bridging phenolates.[129] Rigid back-to-back connection of podand units in $[L21]^{2-}$ also ensures the formation of strict dimetallic complexes $[\{Gd(NO_3)_2\}L21]$ in which two bidentate nitrate anions per Gd(III) complete the coordination spheres.[130] Besides these and related special cases, a large amount of polymetallic f–f[15,18,24,131] and d–f[12,15,20] complexes have been isolated in the solid state in which more or less flexible podand-type ligands bridge two or more metal ions leading to aesthetically appealing solid-state lanthanide-containing clusters whose existence and speciation in solution are largely unexplored (Figure 15). Since crystallization processes select the less soluble candidate of a complete 'dynamic combinatorial library' occurring in solution under a precise set of external conditions,[132] correlations between isolated solid-state structures and thermodynamic parameters responsible for equilibria occurring in solution are often limited and sometimes inadequate. Unfortunately, very few complete speciation and thermo-

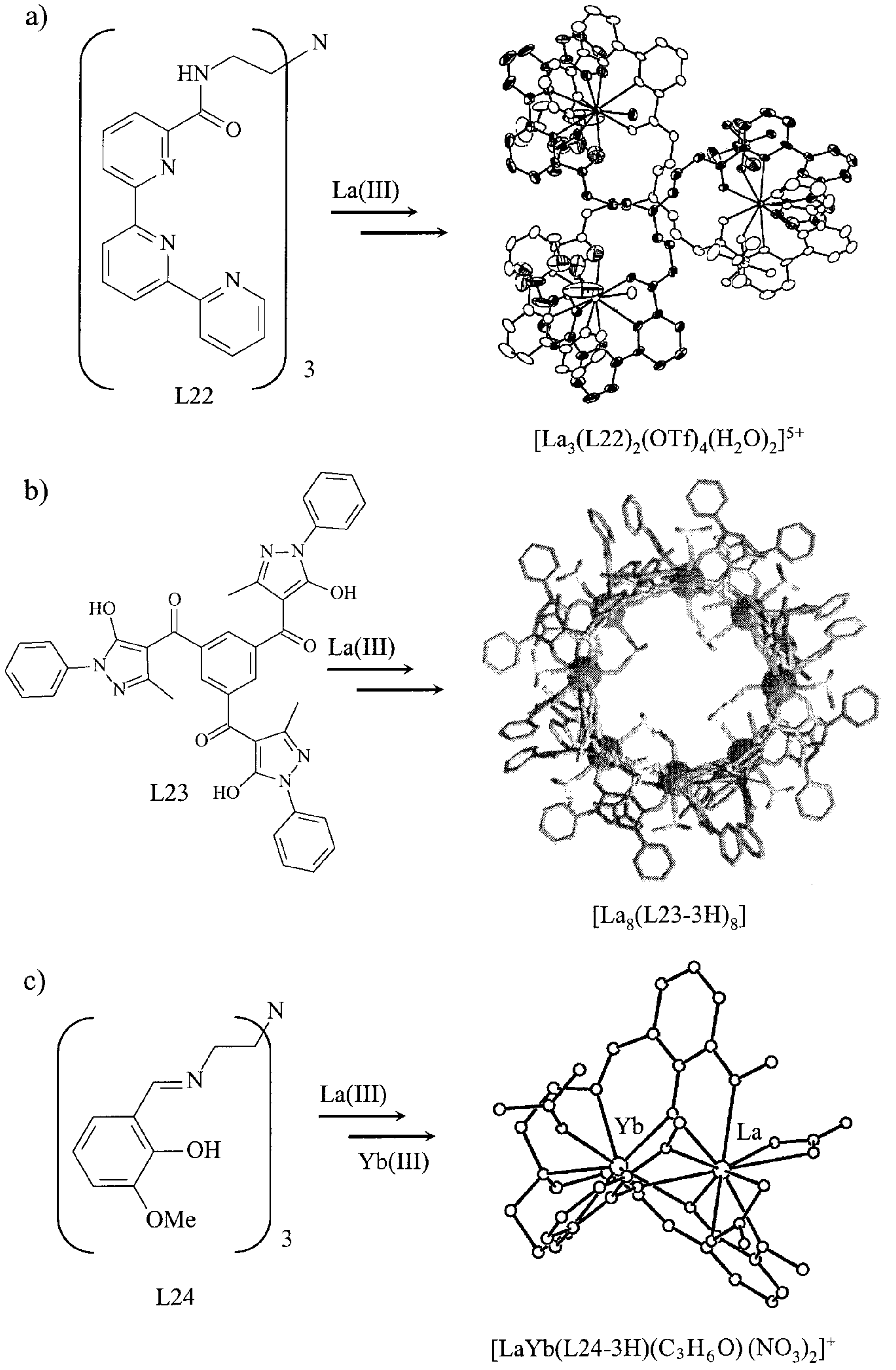
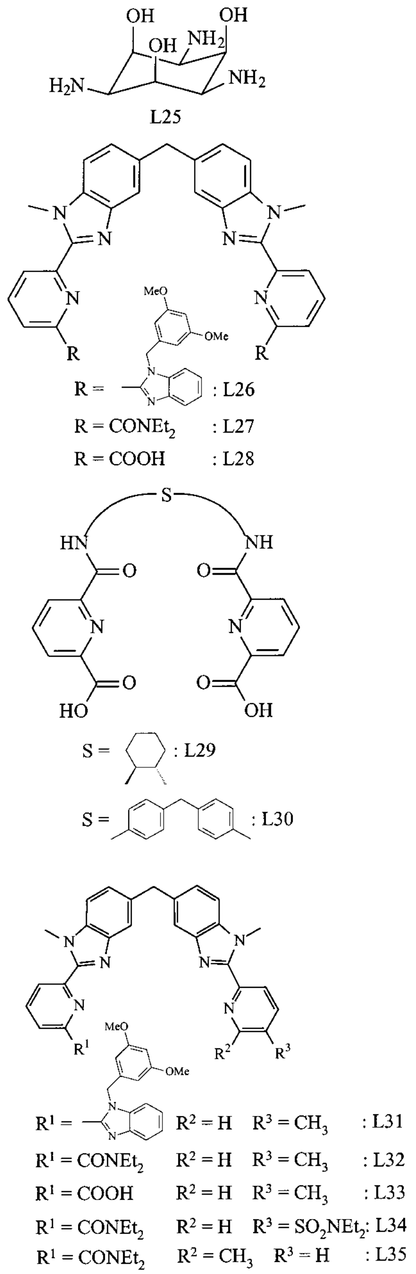


Figure 15. Solid-state lanthanide-containing clusters obtained by crystallization from complicated dynamic virtual combinatorial libraries (adapted from refs 131b (a), 18b (b) and 17 (c)).

dynamic data have been reported for polymetallic lanthanide-containing macrocyclic complexes and podates, and the pioneering work of Inoue and collaborators[121] is a remarkable exception.

A reliable access to thermodynamic parameters becomes essential for the rational design of polymetallic lanthanide-containing complexes with flexible acyclic ligands prepared according to the induced fit concept, because the large degree of freedom of the system prevents simple rationalization of the assembly processes and only a small part of the speciation leading to X-ray quality solid-state aggregates is generally considered.[13,14,133] However, some self-assembly processes involving predetermined ligands and lanthanide-metal ions have been explored in solution.[42,76,134,135] Potentiometric studies of the assembly of L25 (Chart 4) with Eu(III) in water show the exclusive formation of $[Eu_3(L25-3H)_2(H_2O)_6]$ for $7 \leq pH \leq 10$, whereas higher pH induces deprotonation of the coordinated water molecules and polymerization.[134] The absence of complexes with other stoichiometries points to a remarkable predis-

Chart 4



position of the ligands to act as peripheral receptors in the final trimetallic sandwich edifices, two water molecules per Ln(III) completing the coordination spheres (Figure 10a).

The segmental bis-tridentate ligands L26−L28 (Chart 4) represent a series of receptors predisposed for helication and in which terminal groups can be systematically varied without drastically disturbing the assembly process.[76] Ligand L26 has been designed for the first preparation and isolation of triple-stranded helicates $[Ln_2(L26)_3]^{6+}$ in acetonitrile (eq 12, β_{23}).[76a] Limited stability constants result from weak electrostatic point-dipole Ln−N bonds ($\log(\beta_{23}^{Eu}) = 22(1)$) and decomplexation readily occurs in water because ΔH_{11} cannot overcome the large ΔH_{10} expected in the latter solvent. Nevertheless, detailed structural and luminescence studies in acetonitrile and in the solid state demonstrate that the dimetallic triple-stranded helicates $[Ln_2(L26)_3]^{6+}$ are the only detected species, Ln(III) lying in pseudo-tricapped trigonal prismatic sites produced by three wrapped tridentate segments.

$$3Li + 2Ln^{3+} \rightleftharpoons [Ln_2(Li)_3]^{6+} \qquad (12)$$

$$2Li + 2Ln^{3+} \rightleftharpoons [Ln_2(Li)_2]^{6+} \qquad (13)$$

The replacement of terminal heterocyclic nitrogen atoms in L26 by neutral oxygen donors in L27 slightly affects the assembly process. Two complexes with different stoichiometries are detected in solution (eqs 12 and 13), and the stability of the resulting dimetallic helicates $[Ln_2(L27)_3]^{6+}$ in acetonitrile is only marginally increased ($\log(\beta_{23}^{Eu}) = 24(1)$).[76b] The existence of $[Ln_2(L27)_2]^{6+}$, postulated from spectrophotometric data and mass spectrometry in solution, is confirmed by the isolation and structural characterization of the dimetallic side-by-side complex $[Eu_2(L27)_2(H_2O)_2(OTf)_4](OTf)_2$ in the solid state. Although a precise control of the external conditions (stoichiometry, solvent, concentration) is required to selectively produce one particular complex, this example demonstrates that negative cooperativity is compatible with the preparation of well-defined supramolecular complexes.[136] The introduction of negatively charged terminal carboxylates in $[L28-2H]^{2-}$ increases the Ln−ligand bond strength to such an extent that competition with water molecules is overcome, leading to highly stable neutral helicates $[Ln_2(L28-2H)_3]$ in water ($\log(\beta_{23}^{Eu}) = 51(4)$).[76c] A similar behavior has been recently reported for the analogous segmental ligands $[Li\text{-}2H]^{2-}$ (i = 29, 30) which produce $[Ln_2(Li\text{-}2H)_3]$ in water ($\log(\beta_{23}^{Eu}) = 31.6(2)$).[76d]

The synthesis of pure heterodimetallic complexes is more complicated because different segments coded for the selective recognition of one particular metal must be incorporated into predisposed receptors. The segmental bidentate−tridentate ligands L31−L34 have been studied by Piguet and co-workers for their capacities to simultaneously match the stereochemical requirements of Ln(III) (tridentate binding unit) and pseudo-octahedral soft M(II) d-block ions (bidentate binding unit, Figure 16).[42,135] The improved affinity of the tridentate segment for Ln(III) expected when terminal heterocyclic nitrogen atoms (L31) are replaced by oxygen donors in L32 and $[L33\text{-}H]^-$ is indeed observed, but competition between the two different segments for one metal ion complicates the assembly process, and the selective formation of the target helicates (HHH)-$[LnM(Li)_3]^{5+}$ (i = 31, 32, 34; HHH = head-to-head-to-head) and (HHH)-$[LnM(L33\text{-}H)_3]^{2+}$ depends on subtle interplay between steric and electronic (enthalpic terms) and solvation effects (entropic terms). For instance, the affinity of the tridentate bis(benzimidazole)pyridine segment in L31 for M(II) to give $[M(L31)_2]^{2+}$ (M = Fe, Zn) is so strong that the quantitative (>95%) preparation of (HHH)-$[LnM(L31)_3]^{5+}$ in solution obviously requires strict stoichiometric conditions (Ln:M:L31 = 1:1:3), and a large total ligand concentration ($\geq 10^{-2}$ M) is necessary to entropically compensate for this unfavorable

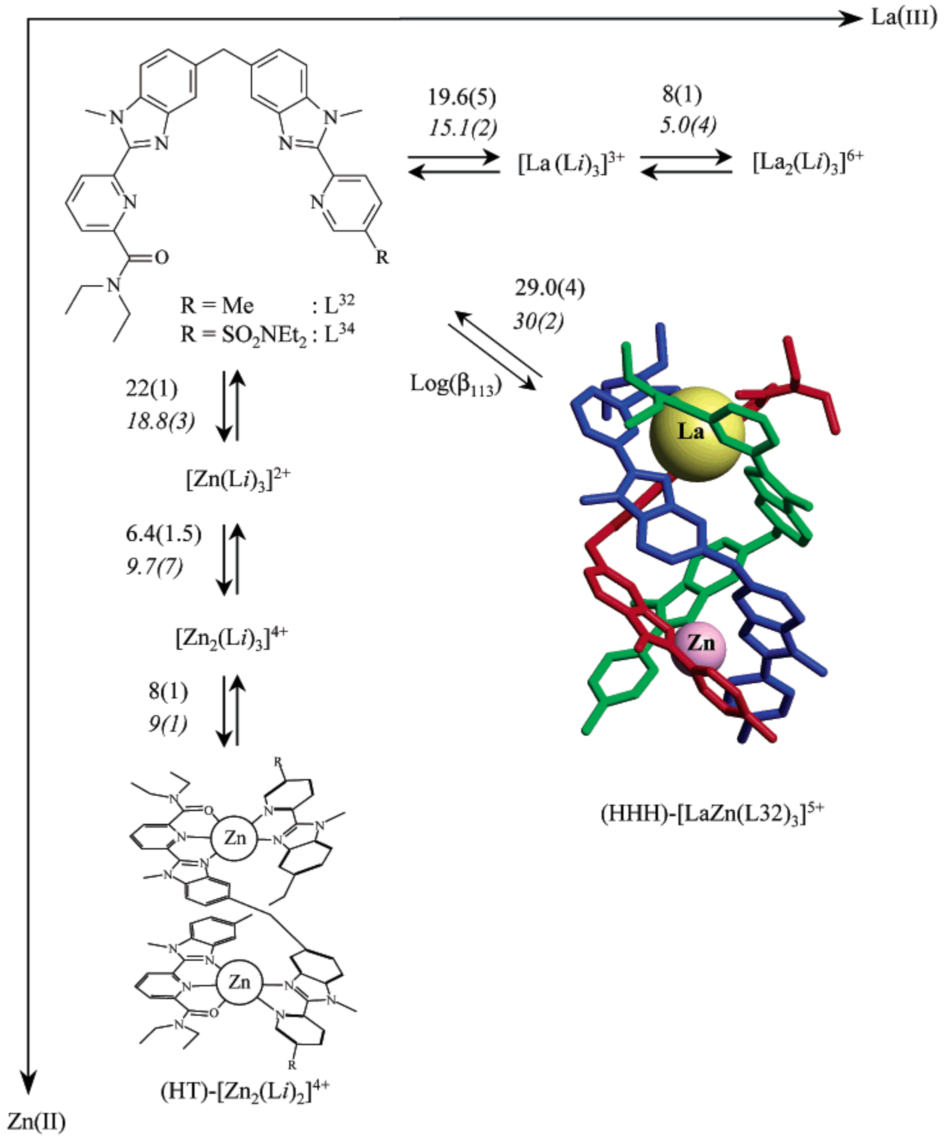


Figure 16. Self-assembly of L32 and L34 with La(III) and Zn(II) in acetonitrile. The stability constant for each defined equilibrium is given as log(K) using regular (L32) and italic fonts (L34) (adapted from ref 42a).

enthalpic contribution. Interestingly, the absolute formation constants log(β_{113}) of the heterodimetallic helicates (HHH)-$[\mathrm{LnM}(\mathrm{L}i)_3]^{5+}$ (i = 31, 32, 34) are comparable for a given set of metals,[42,135] but the selectivity significantly increases (L31 $\ll$ L32 $\approx$ L34) because tridentate NNO binding units display weaker affinity for M(II) in the competition processes. Such fine-tuning of the thermodynamic properties has considerable practical consequences since the luminescent helicate (HHH)-$[\mathrm{EuZn}(\mathrm{L}32)_3]^{5+}$ is quantitatively produced for total ligand concentrations lower than 10^{-4} M while (HHH)-$[\mathrm{EuZn}(\mathrm{L}31)_3]^{5+}$ can only obtained for concentrations larger than 10^{-2} M, a crucial point for the design of sensitive luminescent probes in fluoroimmunoassays.[137]

In favorable cases, thermodynamic programming is reliably traced back to electronic effects, and the remarkable selectivity observed for the formation of (HHH)-$[\mathrm{LaZn}(\mathrm{L}34)_3]^{5+}$ results from electronic σ/π compensation effects induced by the sulfonamide groups bound to the terminal pyridine rings of the bidentate segment, which strongly discriminates between hard Ln(III) (poor affinity associated with σ-attracting effects) and soft Zn(II) (strong affinity associated with retro-π bonding).[135f] Finally, the reliable thermodynamic control of self-assembly processes requires metal ions labile enough to allow a complete dynamic exploration of the energy hypersurface. Lanthanide, alkali, alkaline-earth, and a large part of 3d-block ions are well-suited for this purpose,[95] but some special metal ions with fascinating optical and electronic properties (Cr(III), Co(III), Ru(II), Pd(II), Pt(II)) are often too inert to be used in strict self-assembly processes.[41,138,139] Oxidative (or reductive) postmodifications transforming a labile metal ion into an inert one in a particular oxidation state are valuable alternatives to overcome these limitations. The selective introduction of inert Co(III) (low-spin d^6) into self-assembled triple-stranded helicates (HHH)-$[\mathrm{LnCo}(\mathrm{L}32)_3]^{6+}$ (Ln = La$-$Lu) successfully illustrates this strategy and delivers inert axial lanthanide complexes which are used as structural magnetic probes for advanced developments in paramagnetic NMR (Figure 17).[89d,140]

The tailoring of efficient ditopic ligands able to recognize specifically and simultaneously two differ-

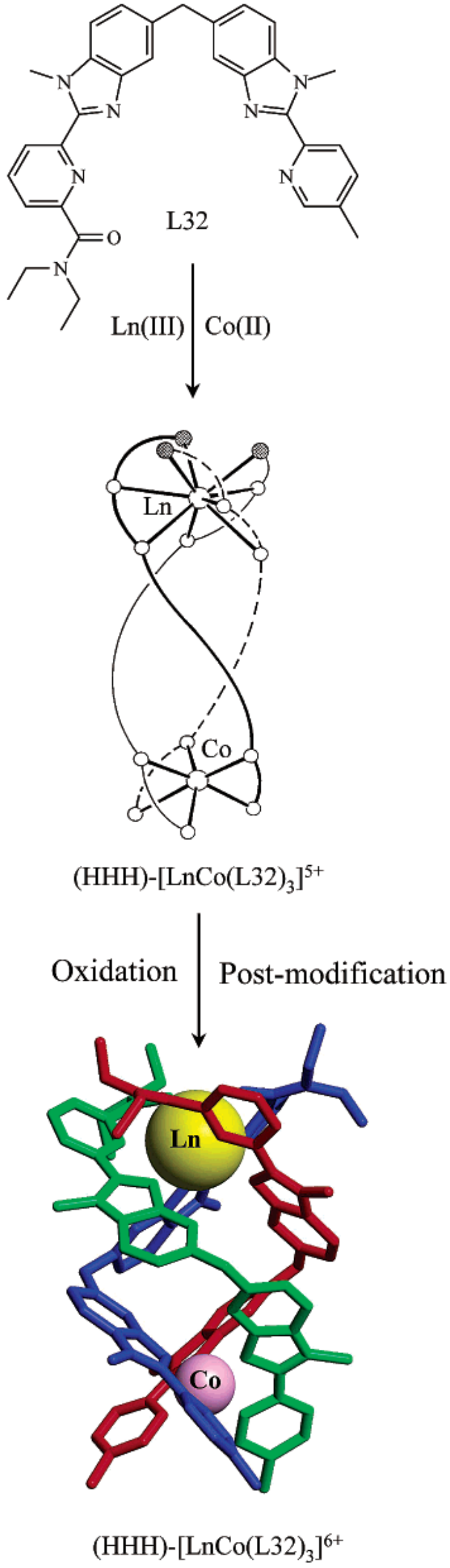
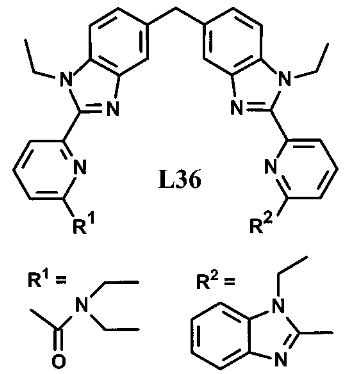
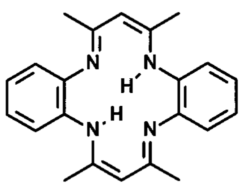


Figure 17. Self-assembly of (HHH)-$[LnCo(L32)_3]^{5+}$ followed by oxidation (postmodification) to give (HHH)-$[LnCo(L32)_3]^{6+}$.

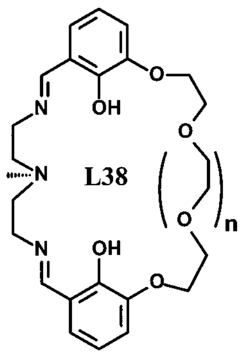
ent lanthanide ions in a strict self-assembly process is even more challenging. Indeed, here the two metal ions lack the substantial differences in hardness and coordination requirements found between a divalent 3d metal and a trivalent 4f ion. Moreover, as stated above, the ion radius difference between two consecutive lanthanides is only minute, which renders invalid any approach based on preorganized, or even predisposed, receptors. On the other hand, if available, heterodimetallic 4f−4f compounds would present exciting properties. This could be exploited, for instance, by combining two luminescent probes in one dimetallic compound for the design of multiple fluoroimmunoassays[30] or by adding a luminescent stain to a magnetic probe for double sensing of a protein domain. Other prospective utilities would include the design of precursors for doped materials with specific magnetic, optical, and electrochemical properties for high-density memory devices.[37] Reacting symmetric ditopic ligands L26-L28 with a mixture of lanthanide salts yields a more or less statistical mixture of homodimetallic (25% + 25%) and heterodimetallic (50%) complexes. Separation either by selective recrystallization or by ion-exchange chromatography is very difficult and has not been attempted, but much as has been done with the ditopic calix[8]arene L13a;[24a] the heterodimetallic species may be identified both in the ES-MS spectrum and by its specific photophysical signature. For instance, terbium-to-europium energy transfer processes have been quantified in both $[Tb_xLn_{2-x}(L13a\text{-}6H)(dmf)_5]$ (Ln = Nd, Eu, Ho)[24a] and $[EuTb(L26)_3]^{6+}$ species.[68a] Crystals for the first X-ray structure reported for a heterodimetallic 4f−4f (La−Yb) podate with (L24−3H) (Figure 15c) were separated from a similar mixture of species.[17] More recently, Bünzli and co-workers came up with an innovative approach and achieved the design of a ditopic ligand able to recognize two different 4f trivalent ions.[141] Considerations based on the thermodynamic properties described in Figure 13 and on subtle differences in the hardness of both the donor atoms and the Ln(III) ions[142] led the authors to synthesize the heteroditopic ligand L36 (Chart 5) bearing one tridentate unit built from a bis(benzimidazole) moiety, which preferentially interacts with the larger, slightly softer Ln(III) ions,[112] as well as one tridentate segment derived from dipicolinic acid diamide, which binds preferentially to the smaller, slightly harder Ln(III) ions.[116] Addition of La(III) to a solution of L36 in acetonitrile results in the formation of the two expected isomers (HHH)-$[La_2(L36)_3]^{6+}$ and (HHT)-$[La_2(L36)_3]^{6+}$. The proportion of the latter (15%) being much smaller than that predicted by pure statistics (75%) points to the La(III) ions preferring a more symmetrical coordination environment. In the presence of a stoichiometric quantity of two different Ln(III) ions, Ln:Ln′:L36 = 1:1:3, both homo- and heterodimetallic species form. For several Ln−Ln′ pairs, however, the proportion of hetero- versus homodimetallic species deviates substantially from the statistical distribution as shown in Figure 18, where the excess of heterodimetallic species ($\Delta x = x_{obs} - x_{stat}$) is plotted versus the ionic radius difference Δr_i for a coordination number of 9.[3] When Δr_i becomes larger than ca. 0.1 Å, an appreciable selectivity develops, the smaller Ln(III) ions being complexed to the harder compartment of the three ditopic ligand strands. Looking into the energetics of the selectivity process, we note that the enrichment obtained for the LaLu pair with respect to $\Delta G°$ for the equilibrium

Chart 5





L37



n = 0: L38a
n = 1: L38b

amounts to $\Delta(\Delta G°) = -7.4$ kJ·mol^{-1} while it decreases below -0.8 kJ·mol^{-1} for $\Delta r_i < 0.1$ Å.[141]

$$[\mathrm{Ln_2(L36)_3}]^{6+} + [\mathrm{Ln'_2(L36)_3}]^{6+} \leftrightarrows 2[\mathrm{LnLn'(L36)_3}]^{6+}, \quad \Delta G° = -3.4\ \mathrm{kJ{\cdot}mol^{-1}} \quad (14)$$

The complexity of assembly processes involving polymetallic edifices (and particularly heteropolymetallic species) leads to the conclusion that the programmed and rational isolation of one particular component out of a dynamic combinatorial library[132] requires a detailed qualitative and quantitative speciation in solution prior to crystallization. Further comparisons between solution and solid-state structures eventually confirm the formation of discrete polymetallic lanthanide-containing edifices and unambiguously establish the (un)favorable role of packing forces.[143] In the next section, we consider discrete polymetallic lanthanide-containing assemblies which are designed for exhibiting specific functions, a step further in complexity since both synthetic and electronic aspects must be simultaneously controlled for different purposes.

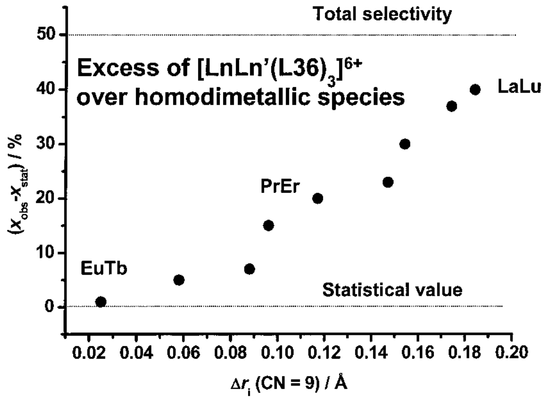
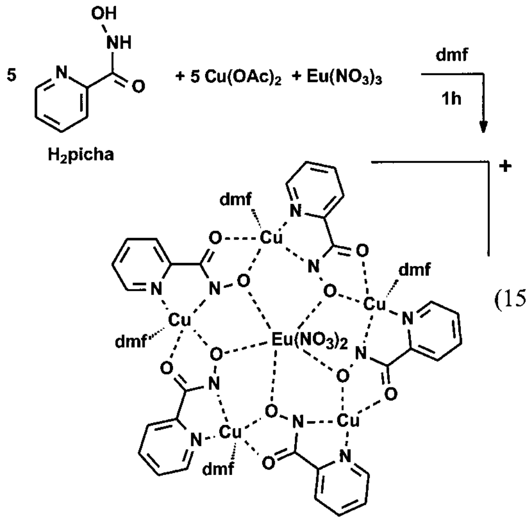


Figure 18. Excess of heterodimetallic species $[\mathrm{LnLn'(L36)_3}]^{6+}$ over homodimetallic species $[\mathrm{Ln_2(L36)_3}]^{6+}$ + $[\mathrm{Ln'_2(L36)_3}]^{6+}$ versus the ionic radii difference of Ln and Ln′. Re-plotted from data in ref 141.

D. Innovative Synthetic Routes to Lanthanide-Containing Polymetallic Assemblies

Building on the principles outlined in the previous sections, authors have worked out new synthetic routes to polymetallic assemblies, using metallacycles either as such, the enhanced—usually magnetic—properties arising from the proximity of several metal ions in the cycle, or as new classes of molecular recognition agents. To our knowledge, this approach was pioneered by Blake et al., who proposed in 1991 new synthetic ways of isolating copper–lanthanide complexes using either a metallacycle[144] or a metal dimer.[145] Metallacrown receptors proposed by Pecoraro et al.[146] work similarly to Pedersen's receptors. Lanthanide encapsulation complexes with copper or nickel metallacrowns are obtained in high yield from one-pot syntheses involving planar ligands such as picoline hydroxamic acid ($\mathrm{H_2picha}$) or nonplanar amino hydroxamic acids, copper (or nickel) acetate, and the appropriate lanthanide(III) nitrate[147]



(15)

In the 15-metallocrown-5 above, four of the five Cu(II) cations are pentacoordinate, being loosely bound to one dmf molecule, while the fifth one is strictly square planar. In all the complexes the Ln(III) ion is generally pentagonal bipyramidal, being coordinated to five oxygen atoms from the metallacycle and solvent or nitrate ions in the axial positions. In the case of Eu(III), two bidentate nitrate ions are bound on either side of the metallacycle. The cavity of the latter presents an estimated radius of 1.2 Å, which matches exactly the Eu(III) ionic radius for a coordination number of nine. The circular arrangement of the d-transition-metal ions implies interesting magnetic properties. For instance, the Gd(NO_3)$_3$ complex of [15-Cu(II)(picha)-5] displays ferromagnetic coupling of the Gd(III) ion to the five Cu(II) ions and its relaxivity is quite large (9.8 mM^{-1} s^{-1} at 20 °C and 30 MHz).[147] Similarly, metallacalixarenes can be synthesized, as shown by recent examples of palladium metallacalix[4]arenes obtained from Pd(II)-en and uracil monoanion[148a] or 4,6-dimethyl-2-hydroxypyrimidine,[148b] which can easily incorporate a La(III)[148a] or Gd(III)[148b] ion.

IV. Functional Polymetallic Assemblies Triggered by Intermetallic Communications

As stated in the Introduction, we primarily review here dimetallic entities containing at least one Ln(III) ion and displaying functional abilities. These can be divided into chemical (acid−base or redox), optical, and magnetic properties. The latter will not be described in detail in this paper, except for our own work in this field, since another review in this issue covers the subject.[21] The classification below relies on the nature of the metal next to the lanthanide in the molecular edifices first and then on the type of intermetallic communication: orbital overlap, electrostatic interaction, mechanical effects. Properties linked to clusters and extended arrays are described in the last section.

A. Edifices Containing 4f- and s-Block Ions

In most of these edifices, the s ion operates either as a counterion, as is commonly seen in organometallic compounds where the Ln(III) and s ions are often linked by a bridging ligand (hydride, chloride, alkyl, binaphthol),[10,39] or as a structure stabilizer, for instance, in the double-decker complex [Li(thf)][Ce(L37−2H)$_2$][149] with the doubly deprotonated crown ether (L37−2H) (Chart 5). Although devoid of any intermetallic interaction, the following compounds are worth mentioning since they open the way for forcing the coordination of a Ln(III) ion to a specific motif of a ditopic ligand, making use of differences in the chemical properties of s and 4f ions. Compartmental Schiff-base macrocyclic ligands have long be used to produce dimetallic f−d and f−f complexes.[15,16] Recent work has shown that an asymmetric ligand containing one N_3O_2 Schiff base and one O_2O_3 or O_2O_4 (L38, Chart 5) “crown-like” coordination moiety coordinates Ln(III) ions into the crown ether chamber.[150] The same compartment also traps alkali and alkaline-earth ions. When reacted with the resulting complexes, the Ln(III) ions are unable to displace the s ions and bind into the Schiff-base compartment, yielding for instance, [YbNa(L38a-2H)]$^{2+}$ (Yb···Na contact distance = 3.555(2) Å)[151] or [LaBa(L38b-2H)]$^{3+}$ [150] dimetallic entities.

Typical examples of s-4f functional entities have been mentioned earlier and are described in Figures 7a and 8. In both examples, the presence of the s ion(s) in the polymetallic edifices induces changes in the photophysical[75] or relaxivity[80−82] properties of the Ln(III) ion. Let us turn to the development of sensitive analytical lanthanide-containing fluorosensors.[152] Luminescence of the metal ion may be either enhanced or quenched by the presence of the analyte.[153] The former process was used in the design of the supramolecular potassium sensor depicted in Figure 7a and comprised of three units.[75] The central one is a terpyridine-based moiety for the complexation of the luminescent sensing ion, Eu(III); the outer macrocycles are good complexing agents for potassium, and they are connected to the terpyridine unit by a phenyl group acting as an electronic relay which conveys electronic density from the nitrogen lone pairs located on the monoazacrown-6 ethers toward the central unit. In the absence of potassium, a photoinduced electron transfer (PET) operates, which reduces the Eu(III) ion and quenches its luminescence: the quantum yield in methanol is as low as 2.6%. Upon potassium complexation the lone-pair electron density is attracted by the positive charge of the cation and the PET process no longer occurs. As a result, the quantum yield jumps to 46% when two K(I) ions are bound.[75] Building on this principle, molecular photoionic and logic gates with bright luminescence and on−off digital action may be programmed.[154] Another example of supramolecular luminescent sensors is the dota-based Eu(III) and Tb(III) complexes bearing a specific substituent for the complexation of alkaline-earth metal ions and described in Figure 19.[155] The photophysical properties (absorpion and emission spectra) of the [Ln(L39−3H)] macrocyclic chelates are modulated by alkaline-earth metal and zinc complexation. For instance, zinc binding induces luminescence enhancements of 26% and 42% for Tb(III) and Eu(III), respectively, meaning that the luminescent lanthanide probe senses the presence of the other metal ion in the corresponding complexation unit. This enhancement can be related to the suppression of a photoinduced electron transfer from the benzylic nitrogen to the intermediate aryl singlet excited state upon M(II) complexation, thus modifying the energy transfer processes within the molecule and favoring energy migration onto the Ln(III) ion. Moreover, the supramolecular sensor turned out to be highly selective for Zn(II) over Ca(II) and Mg(II), as shown by log β_{ML} values for the Tb(III)

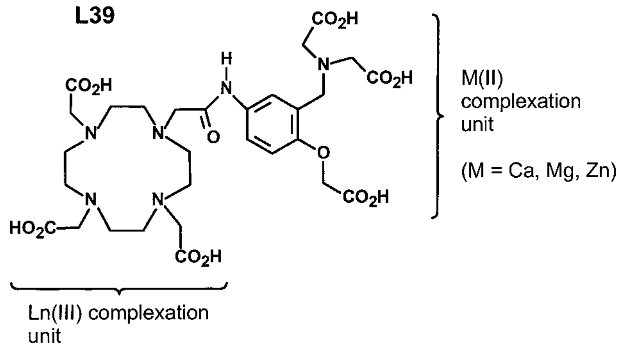


Figure 19. Design of a M(II) ion-selective luminescent sensor.

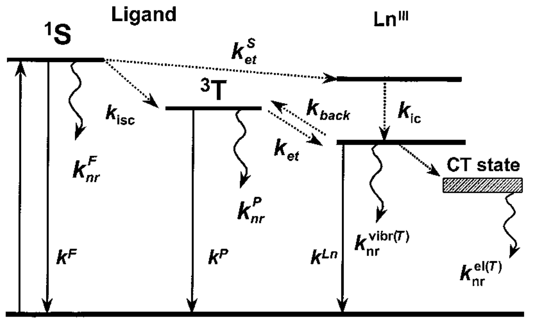


Figure 20. Schematic diagram showing the energy migration paths in a Ln^{III} complex (^{1}S = singlet state, ^{3}T = triplet state, F = fluorescence, P = phosphorescence, isc = intersystem crossing, nr = nonradiative, ic = internal conversion, et = energy transfer, back = back transfer, T = temperature-dependent, el = electronic, vibr = vibrational, CT = charge transfer). For a detailed discussion, see ref 159.

complex, which decrease from 5.48 for Zn(II) to 3.84 and 2.0 for Ca(II) and Mg(II), respectively.[155]

B. Edifices Containing 4f- and d-Block Ions

These edifices are among the most numerous and most studied lanthanide-containing polymetallic compounds, particularly the 3d−4f entities,[10,11,15,16] for which the three types of intermetallic communication mentioned above are taken advantage of.

1. Communication Based On Orbital Overlap

This type of intermetallic interaction is mainly involved in the magnetic coupling of d- and f-transition-metal ions, which has focused much attention in view of attempts to design molecular magnets. Due to the restricted expansion of the f-orbitals though, this coupling is usually quite small;[12] for instance, the Cu(II)−Gd(III) coupling is very often ferromagnetic with an exchange integral on the order of a few (1−10) cm^{-1}.[15,22b,156−158] For more details, see the review by Gatteschi and Benelli.[21]

In edifices containing luminescent Ln(III) ions, orbital overlap may also influence the flow of energy through the various transfer processes occurring in such molecules.[159] Figure 20 presents the main processes involved and points to the complexity of the Ln(III) ion sensitization by the surrounding ligands (f−f transitions have too weak an oscillator strength to act as an efficient Ln(III) excitation path in molecular compounds). Typically energy is absorbed by one of the ligand excited singlet states, partially transferred onto the lowest triplet state before migrating onto one (or several) of the numerous Ln(III) excited states. Nonradiative de-excitation of the long-lived luminescent excited state of the Ln(III) ion occurs through vibrational relaxation or internal conversion. When the Ln(III) ion is close to an entity with which it may potentially interact via orbital overlap or when an efficient electronic relay is present, as discussed in the preceding section, mixing of the 4f orbitals with ligand or d-transition-metal orbitals creates faster relaxing states and lowers the f-state emission probability. For instance, mixing of the 4f orbitals with low-lying charge-transfer states produces an important quenching of the Ln(III)-centered luminescence if the redox potential of the Ln(III) ion is low, which is the case for Eu(III). Energy may also be trapped by the d-transition-metal ion and then dissipated by nonradiative paths. This is what mainly happens in most of the 3d−4f complexes isolated with Schiff bases and in which the Ln(III)−M(II) contact is usually in the range 3.2−3.6 Å. The fact that both Eu(III) and Tb(III) luminescence is quenched is indicative of energy trapping by the 3d metal ion. Documented examples involve, among other ions, V(IV), Cr(III), Co(III), Ni(II), and Cu(II).[15,160]

2. Electrostatic Communication

Energy transfer processes involving lanthanide ions can also occur through multipolar (mainly dipolar) through-space mechanisms. Of the systems investigated to date, multipolar energy transfer following the Förster−Dexter model seems to be the most common mechanism.[161,162] The main point here, besides the strength of the donor−acceptor interaction, is the dependence of the rate of energy transfer on the spectral overlap between the normalized donor emission spectrum $D_e \rightarrow D_g$ and normalized acceptor absorption spectrum $A_e \leftarrow A_g$

$$W_{DA} = \frac{2\pi}{\hbar}\cdot|\langle D_gA_e|\mathbf{H}_{DA}|D_eA_g\rangle|^2\cdot\int g_D(E)g_A(E)\,dE \tag{16}$$

where the subscripts g and e refer to the ground and excited electronic states of the donor D and the acceptor A, $\mathbf{H_{DA}}$ is the Hamilton operator for the multipolar D−A interaction, and $g_D(E)$ and $g_A(E)$ are the normalized line-shape functions of the transitions. For a dipole−dipole mechanism, the dependence with respect to the D−A distance is proportional to $(R_{DA})^{-6}$,[161] and appreciable transfers up to 10−15 Å are common. The yield η of the transfer is given by the simple relationship

$$\eta = 1 - \frac{\tau}{\tau_0} = \frac{1}{1 + \left(\frac{R_{DA}}{R_0}\right)^6} \tag{17}$$

where τ and τ_0 are the donor excited-state lifetimes in the presence and in absence of the acceptor (the lifetime of which is unaffected by the transfer process) and R_0 is the donor−acceptor distance for which the yield of transfer amounts to 50%. The equation is only valid when the donor luminescence decay is a single exponential. Through-space 4f → 3d (or 3d → 4f) energy transfer processes have been studied on molecular solids containing tris(dipicolinato) lanthanide anions with general formula $[ML_x][Ln(dipic)_3]\cdot nH_2O$ (M = Cr(III), Co(III), L = urea or various amines).[74] In these systems, the Ln−M distance is around 6.5−7.5 Å and precludes any orbital overlap between the two ions, even through electronic relays, since the two metals are embedded in separate coordination entities. With respect to $Cs_3[Eu(dipic)_3]$ (dipic = L9−2H) which is highly luminescent, the Eu(III) emission is quenched in both heterodimetallic entities, as is easily understandable from Figure 21.

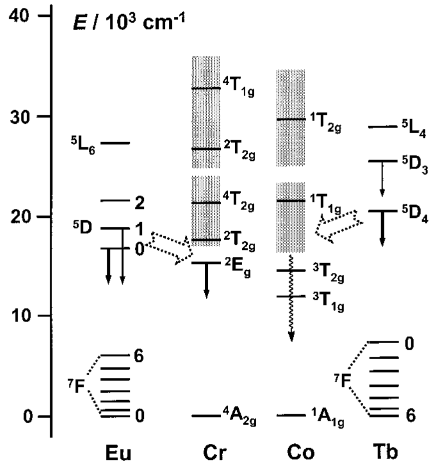


Figure 21. Energy level diagram showing 3d states of Cr(III) and Co(III) and 4f states of Eu(III) and Tb(III). Down-pointed arrows tag luminescent states, while the broad, dotted arrows show the main quenching paths of the Ln-centered luminescence. (Redrawn from ref 74.)

Indeed, both Cr(III) and Co(III) have levels almost resonant with those of Eu(III) and Tb(III), whose emission is also quenched. The Eu(III) lifetime in the Co(III) assemblies is too small to be measured, pointing to a transfer yield close to 100%, while a yield of 95% is estimated for the Cr(III) compounds. In fact, since Cr(^2E_g) is a luminescent state, Cr(III) luminescence is seen, so that the compounds act as double light-converting devices. When d-transition metals having no electronic levels in the range 18–35 000 cm^{-1} are used, e.g., Rh(III), the Ln(III) luminescence remains unaffected, which really proves the above-described energy transfer mechanism.[74a] At this stage, it is worth noting that Cr(III) is used as a sensitizer in several lanthanide-containing solid-state devices to induce near-infrared emission of Nd(III), Er(III), or Tm(III).[23a]

Demonstration of the tuning of long-range 3d–4f interaction is made by recently published M(II)–Ln(III) (M = Zn, Fe) heterodimetallic systems based on ligands L32 and L35 (Chart 4). The divalent iron $3d^6$ ion is a promising versatile acceptor in heterodimetallic 3d–4f complexes in view of its two possible electronic configurations with different electronic (optic and magnetic) properties depending upon the ligand-field strength around Fe(II). The (HHH)-$[LnFe(L32)_3]^{5+}$ helicates, in which the three bidentate units of the three ligand strands are coordinated to the Fe(II) ion, indeed display spin crossover behavior between the Fe(II) $^1A_1$ and $^5T_2$ electronic configurations along with thermochromism. The low-temperature, low-spin diamagnetic form is violet, while the high-temperature, high-spin paramagnetic form is orange.[135f] The color of the former is due to an intense metal-to-ligand charge-transfer (MLCT) absorption located at 19 000 cm^{-1} ($\epsilon = 5800\ M^{-1}\ cm^{-1}$) and which totally quenches the Eu(III) luminescence via an efficient Eu(III) → Fe_{ls}(II) energy transfer (the La–Fe contact is around 9 Å).[135e] On the other hand, the MLCT band of the high-spin form lies at much higher energy (around 23 000 cm^{-1}, $\epsilon \approx 1000\ M^{-1}\ cm^{-1}$) and is of lower intensity, so that Eu(III) luminescence should be observed. However, a sufficiently large high-spin fraction cannot be attained in the accessible temperature range, and no lanthanide-centered luminescence is observed.[135e,135f] Displacement of the methyl substituent connected to the 5 position of the pyridine ring (L32) to the 6 position in L35 prevents the contraction of the Fe(II)–N bonds required for the formation of low-spin Fe(II) helicates, and pure high-spin compounds (HHH)-$[LnFe(L35)_3]^{5+}$ are obtained.[42b] The weak MLCT transition is located at 22 200 cm^{-1} ($\epsilon \approx 500\ M^{-1}\ cm^{-1}$), while the spin-allowed 3d–3d transitions appear in the range 8800–11 000 cm^{-1} ($\epsilon = 11–14\ M^{-1}\ cm^{-1}$). Therefore, in these compounds, high-spin Fe(II) provides a semitransparent spectral windows in the range 12–20 000 cm^{-1}, therefore minimizing somewhat the long-range intramolecular Eu(III) → Fe(II) transfer which is so efficient in $[EuFe(L32)_3]^{5+}$ (see Figure 7b). As a result, $[EuFe(L35)_3]^{5+}$ is luminescent, although weakly, its quantum yield upon ligand excitation being about 300 times smaller than the one of the corresponding Zn(II) compound.[42b] This situation is illustrated in Figure 22, and the main outcome of this work is that Eu(III) may act as a luminescence reporter of the iron spin state.

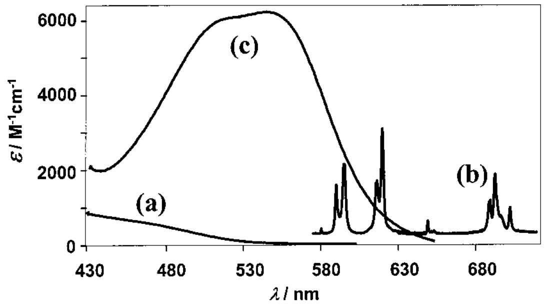


Figure 22. Comparison between (a) the absorption spectrum (acetonitrile, 298 K), (b) the emission spectrum (solid state, 13 K) of high-spin $[EuFe(L35)_3]^{5+}$, and (c) the absorption spectrum of low-spin $[EuFe(L32)_3]^{5+}$ (acetonitrile, 298 K) showing the semitransparent spectral window provided by the former compound. (Redrawn from ref 42b.)

Finally, electrostatic communication between d- and f-block ions has been shown to affect the electrochemical potentials of metal-centered oxido-reduction processes.[89d,163] For instance, Co(II) oxidation is delayed by 60 mV when Ln(III) replaces Co(II) in the appended site in the triple-stranded helicate (HHH)-$[LnCo(L32)_3]^{5+}$. Detailed calculations lead to a relative dielectric permittivity of $\epsilon_r \approx 30$, typical for triple-stranded helicates in which solvent molecules do not penetrate the intermetallic region.[89d] Similar anodic shifts have been used for sensing Ln(III) in heterodimetallic calixarene complexes containing a ferrocene reporter.[163]

3. Mechanical Coupling

Intermolecular mechanical coupling between metallic centers in solid-state networks is well established, particularly for Fe(II) complexes for which magnetic hysteresis loops depend on cooperative spin-crossover processes.[164] Recent extensions toward controlled mechanical coupling in heteropolymetallic networks containing s- and d-block ions have been proposed,[165] but very few attempts have been made

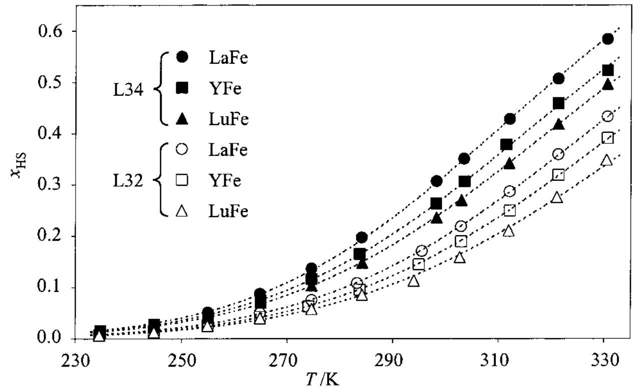


Figure 23. Mole fraction (x_{hs}) of high-spin Fe(II) ($^5T_2$) for the thermal spin-crossover transition occurring in (HHH)-$[LnFe(Li)_3]^{5+}$ (i = 32, 34; acetonitrile; 233−333 K). Dotted lines are calculated with the thermodynamic data given in Table 2. (Redrawn from ref 135f.)

Table 1. Thermodynamic Parameters for the Fe(II) $^1A_1 \leftrightarrow {}^5T_2$ Spin-State Equilibria Observed for (HHH)-$[LnFe(Li)_3](ClO_4)_5$ (i = 31, 32, 34) in Acetonitrile, as Obtained from Magnetic Measurements

compound	ΔH_{sc}/ kJ mol^{-1}	ΔS_{sc}/ J mol^{-1} K^{-1}	T_C[a]/K	R[b]/Å	ref
$[LaFe(L31)_3]^{5+}$	20.6(6)	57(3)	361(8)	1.216	135b
$[SmFe(L31)_3]^{5+}$	20.0(9)	55(4)	364(8)	1.132	135b
$[LaFe(L32)_3]^{5+}$	30.0(2)	88(1)	339(5)	1.216	135f
$[YFe(L32)_3]^{5+}$	29.8(3)	86(1)	345(5)	1.075	135f
$[LuFe(L32)_3]^{5+}$	28.9(4)	82(2)	353(4)	1.032	135f
$[LaFe(L34)_3]^{5+}$	30.1(2)	94(1)	320(5)	1.216	135f
$[YFe(L34)_3]^{5+}$	29.2(2)	89(1)	327(4)	1.075	135f
$[LuFe(L34)_3]^{5+}$	28.8(2)	87(1)	331(3)	1.032	135f

[a] Critical temperature for which $x_{hs} = 0.5$ ($T_C = \Delta H_{sc}/\Delta S_{sc}$). [b] Effective ionic radii for nine-coordinate Ln(III).[8]

to incorporate 4f-block ions.[13] As far as discrete oligomers are concerned, mechanical coupling has been studied in homopolymetallic p- and d-block ions,[166] but its unambiguous demonstration in complexes possessing d- and f-block ions relies on the triggering of Fe(II) spin-crossover properties in the heterodimetallic triple-stranded helicates (HHH)-$[LnFe(Li)_3]^{5+}$ (i = 31, 32, 34, Chart 4).[135] In these complexes Fe(II) is coordinated by six heterocyclic nitrogen atoms in trigonally distorted octahedral environments (as described for Zn(II) in (HHH)-$[LnZn(L32)_3]^{5+}$, Figure 16) which provide ligand-field strengths compatible with Fe(II) $^1A_1 \leftrightarrow {}^5T_2$ spin-state equilibrium occurring around room temperature. Detailed analysis of the low-spin ↔ high-spin transition in (HHH)-$[LnFe(Li)_3]^{5+}$ (i = 32, 34) shows that the fraction of Fe(II) high spin at a given temperature (x_{hs}) depends on the size of the lanthanide ion coordinated in the neighboring site (Figure 23).[135d,135f] The thermodynamic parameters ΔH_{sc} and ΔS_{sc} associated with the spin-crossover processes give some insight into the origin of the mechanical coupling responsible for the communication between the metallic sites (Table 1).

Table 2. Interaction Parameter *J* for Trivalent Gd−Gd Pairs in Several Dimetallic Edifices, as Calculated by the Spin-only Model of Heisenberg (Eq 18)

compound	bridging units	Gd−Gd distance/ pm	g	J/cm^{-1}
$Gd_2(AcO)_2(phen)_2$[a]	$2CH_3CO_2^-$	n.a.	2.00	−0.053
$Gd_2(L42\text{-}4H)(NO_3)_2\cdot 4H_2O$[b]	$2C_6H_5O^-$	n.a.	1.975	−0.211
$Gd_2L_2\cdot 2CHCl_3$[c]	$2C_6H_5O^-$	398	2.00	−0.045
$Gd_2(L24\text{-}3H)(NO_3)_3\cdot 3H_2O$[d]	$3C_6H_5O^-$	(360)[e]	1.999	−0.104
$Gd_2(L''\text{-}3H)_2\cdot 4dmso$[f]	$2C_6H_5O^-$	386	1.98	−0.073
$[Gd_2(L13a\text{-}6H)]\cdot 5dmf$[g]	$2C_6H_5O^-$ 1dmf	366	1.97	−0.063

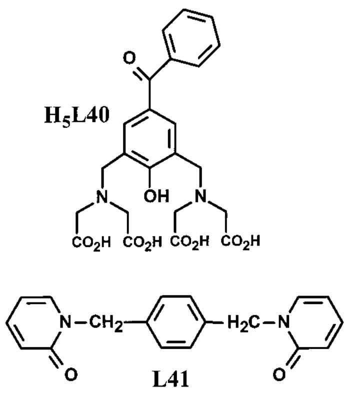
[a] From ref 184. [b] From ref 185. [c] L = tris{[2-hydroxybenzyl)-amino]ethyl}amine.[186] [d] From ref 17. [e] Estimated from the Yb−La structure.[17] [f] L″ = *p-tert*-butylcalix[5]arene.[187] [g] From ref 187.

The initial ligand L31 only poorly coordinates to Ln(III) and leads to flexible lanthanide sites in (HHH)-$[LnFe(L31)_3]^{5+}$ which induce negligible steric constraints on the extension of the Fe−N bonds required for the spin-crossover process (ΔH_{sc} = 20.0−20.6 kJ·mol^{-1} for (HHH)-$[LnFe(L31)_3]^{5+}$ [135b] can be compared to ΔH_{sc} = 20.1(8) kJ·mol^{-1} for the monometallic complex $[Fe(5\text{-methyl-2-(2-methylbenzimidazol)pyridine})_3]^{2+}$).[167] The replacement of the terminal benzimidazole group of the tridentate binding unit in L31 by a carboxamide group in L32 and L34 improves its affinity for Ln(III). The resulting rigid pseudo-tricapped trigonal prismatic lanthanide site contributes to the organization, rigidification, and wrapping of the strands about Fe(II). The enthalpic contributions to the Fe−N expansion in (HHH)-$[LnFe(Li)_3]^{5+}$ (i = 32, 34) are similar, but they increase by ca. 10 kJ·mol^{-1} compared to the noncoupled systems (Table 1). Moreover, the slight but significant decrease of ΔH_{sc} with decreasing size of Ln(III) demonstrates that the intermetallic d−f mechanical coupling mediated by the ligand strands allows the fine-tuning of the Fe(II) magnetic and optical properties. Finally, the attachment of an electron-withdrawing sulfonamide group at the 5-position of the terminal pyridine ring in L34 has negligible effects on the ligand-field strength due to σ/π compensation effects, but the overall decrease of the critical temperature (T_c) results from specific entropic effects induced by ion pairing in the low-spin state.[135f]

C. Edifices Containing Two (or More) 4f-Block Ions

As stated in section III.C, many strategies have been used to design polymetallic f−f molecular entities. Bis(macrocyclic) ligands are an obvious choice, although they result in two f ions located at a long distance from each other, reducing possible communication between them. Typical examples are bis(15-crown-5) derivatives,[168] bis(calixarenes),[169] or bis(cyclen) derivatives.[120] Trying to bring the two ions closer together led several authors to use large, predisposed, and flexible macrocycles based on Schiff bases or calixarene frameworks (L12−L16), Chart 2,[121−125,170] or on macrotricyclic units.[171,172] An alternative is to sandwich the two ions between two macrocycles, with small ligand molecules (hydroxyl groups, chlorides, dmso molecules) acting as bridging units; examples are complexes with para-substituted

Chart 6



H_5L40

L41

calix[5]arenes[173,174] or with porphyrins and phthalocyanins[175] (but triple-decker complexes see the f-ion separation increased by the insertion of a ligand molecule between them[37,176]), while *cis*-inositol L25 yields trimetallic complexes.[177] Lanthanide-templated reactions may also be used to produce polymetallic complexes, especially with cyclic Schiff bases.[178] Finally, careful design of functional 4f−4f edifices may take advantage of self-assembly processes, for instance, with H_5L40 (Chart 6) to yield homo- and hetero-dimetallic chelates[24d] or with L26-L30,[76] L36,[141] L41[133a] to produce triple-stranded dimetallic helicates. Ligand-controlled self-assembly of polymetallic lanthanide-containing clusters featuring oxo and/or hydroxo bridges has also been recently proposed.[179] The dimetallic edifices often have improved chemical or physicochemical properties over the monometallic ones. For instance, in catalysis, (i) facile oxidation of phenols in the presence of a dicerium(IV) complex of calix[8]arene was demonstrated[180] and (ii) improved rates were found for the cleavage of phosphodiester bonds in DNA and RNA (see section II.A). The redox potential may also be affected, as shown by the dimetallic Eu(III) complex of an octaazacyclohexacosane octaacetic acid macrocycle which undergoes a two-electron reduction to Eu(II) at a more cathodic potential than the one-electron reduction of the monometallic complex.[181] Mixed oxidation state species Ln(II)−Ln(III) have also been isolated (particularly with Yb and Sm), for instance, with a terbutylated pyrazolate.[182] Generally speaking, interest for 4f−4f polymetallic species mainly lies, in addition to improved catalytic efficiency, in the fine-tuning of magnetic and spectroscopic properties as well as in the design of precursors for lanthanide-based materials.[35a]

1. Communication Based On Orbital Overlap

For reasons exposed previously (see Figure 1), 4f-orbital overlap is not expected to be substantial when the distance between two Ln ions is larger than 3.5−4 Å, which is the case in molecular edifices. As an illustration, only weak magnetic interactions are reported in di- or polymetallic 4f-containing compounds. Exchange interactions between two paramagnetic centers with well isolated orbital singlets is described by the Heisenberg model with the spin Hamiltonian

$$\hat{H} = -\frac{2J}{\hbar^2}\hat{S}_1\cdot\hat{S}_2 \qquad (18)$$

where J is the exchange parameter which takes negative values for an antiferromagnetic coupling and positive values for a ferromagnetic interaction. In the case of Ln ions, however, orbital contributions to the magnetic moment are usually large (except for $4f^7$) and the spin−orbit coupling is important while the ligand field is weak. A complete treatment of magnetic interactions cannot make simple use of eq 18, and a wealth of parameters have to be introduced. Models have been developed, for instance, for a dimetallic compound having lanthanide ions with an odd number of electrons and assuming cubic ligand fields. In this case, the highest temperature at which the magnetic susceptibility is maximum is expected in the case of $4f^7$ (Gd(III)), $4f^5$ (Sm(III)), and $4f^9$ (Dy(III)), in line with experimental data on $[Ln(C_5H_5)_2Br]_2$.[183] The magnetic behavior of Gd−Gd ($4f^7$) pairs is documented for several systems in which the metal ions are connected by bridging ligands, for instance, in coordination compounds,[184,185] podates[17,186] or complexes with calixarenes.[187] The examples listed in Table 2 show that the interaction is antiferromagnetic, with coupling constants J in the range −0.045 to −0.2 cm^{-1}, which is at least 1 to 2 orders of magnitude lower than that for Gd−Cu pairs, for instance. Interaction in trimetallic Gd(III) compounds is on the same order of magnitude ($J \approx -0.1$ cm^{-1}).[134,188]

2. Electrostatic Communication

Dipole−dipole interaction between two lanthanide ions located at a relatively long distance also influences the magnetic properties of the dimetallic entity. However, there are few investigations addressing this problem. In one case though, dealing with a dimetallic Gd(III) complex of a 34-membered macrocycle, the dipolar field strength generated by one ion at the other paramagnetic site (distance of 10.89 Å) was calculated to be 57 G and made responsible for the absence of hyperfine structure in the EPR spectrum.[121]

Most of the work dealing with dipole−dipole interaction focuses on luminescent properties and energy transfer processes. Resonant energy transfer has been used to characterize the nature of Ln−Ln interactions in solution and to probe the existence of polymetallic complexes.[189] A major application of these Förster-type energy transfers emerged around 1975 when they started to be used to determine the distances separating metal-ion sites in large biological molecules.[63] Indeed, calcium and zinc may easily be substituted by Ln(III) ions which have similar ionic radii and water exchange rate. Introduction of a pair of different Ln(III) ions (e.g., Tb and Nd or Ho) in two different sites and measurement of the lifetime of the donor (Tb) in the presence and absence of the acceptor allows one to calculate their separation provided R_0 is known (see eq 17). Getting a good estimate of the latter is however not easy a task since several parameters are involved

$$R_0{}^6 = 8.78 \times 10^{-25}\kappa^2 Q_D n^{-4} J_{ov} \qquad (19)$$

where κ^2 is an orientation factor with an isotropic limit of 2/3, Q_D is the quantum yield of the donor in the absence of acceptor, n is the refractive index, and J_{ov} is the normalized overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor. Although most of the parameters involved in eq 19 can be accessed experimentally, more dependable values of R_0 are obtained from systems for which an X-ray structure is available. Values for several Eu−Ln (Ln = Pr, Nd) and Tb−Ln (Ln = Pr, Nd, Ho, Er) pairs have been proposed in the case of thermolysin, for which reliable distances between the two closest calcium sites were obtained (11.7 Å); they are in the range 8.2−8.5 Å for Eu(III) and 7.8−9.3 Å for Tb(III). It should be noted that a change in $R_0{}^6$ by a factor two leads to a distance estimate differing only by 12%.[190] More recently, this technique was used to characterize the structure of the EF-hand protein S100-beta containing two helix−loop−helix binding motifs, the distance of which was calculated to be 15 ± 0.4 Å from a resonance energy transfer experiment between Eu(III) and Nd(III).[191]

Dimetallic edifices containing two different lanthanide ions may be used either as light-converting devices, for instance, when the luminescence of a given Ln(III) ion is difficult to sensitize (e.g., Nd), or as model molecules to test the energy migration mechanisms. Referring to the latter, the Tb → Ln (Ln = Nd, Eu, Ho) energy transfer processes have been investigated in Ln-doped Tb(III) crystalline dimetallic complexes of *p*-*tert*-butylcalix[8]arene (L13a).[24a] In these compounds, the intramolecular Tb−Ln distance is around 3.7 Å (estimated from the crystal structure of the Eu compound) while there are several intermolecular distances, the shortest one being 11 Å. In fact, a simple dipole−dipole model taking into account these two types of interacting Tb−Ln pairs satisfactorily explains the lifetime data, and the intermolecular Ln−Ln distance is reproduced accurately for the three systems investigated with $R_0 = 9$ Å. The efficiency of the intramolecular energy transfer process ranges between 65% and 85%. Similar yields have been obtained for intramolecular Eu → Nd energy transfers in dimetallic complexes with *p*-nitro-calix[8]arene (L13b).[24b] In a related study with L14, Kahwa and co-workers showed that R_0 amounts to 7.3 Å for the Eu−Sm pair. On the other hand, an investigation on dimetallic complexes of a biscalix[4]arene in solution was less conclusive because of solvent effects, but the yield of the Eu → Nd energy transfer could be estimated as being in the range 51−66%, depending on the solvent.[123] Luminescence spectra and lifetimes allow the discrimination between homo- and heterodimetallic species. For instance, when a self-assembly process is initiated between L26 and Eu(III) or Tb(III), the resulting homodimetallic triple-stranded helicates display a monoexponential luminescence decay. On the other hand, if the self-assembly process is conducted with equivalent amounts of Ln and Ln′, a mixture of homo- and heterodimetallic helicates is obtained, which is characterized by a biexponential luminescence decay; one lifetime corresponds to the Ln(III) ions in the homodimetallic entity, while the other is characteristic of the Ln−Ln′ pair. From lifetime data, the yield of the Tb → Eu energy transfer could be estimated to 76% in $[EuTb(L26)_3]^{6+}$, with R_0 equal to 10.4 Å.[76a]

3. Mechanical Coupling

As discrimination between Ln(III) with different sizes is a prerequisite for the selective recognition of lanthanide ions and the preparation of heteropolymetallic f−f complexes, it is surprising that very little interest has been focused on the elucidation of mechanical coupling mediated by the ligand backbone. Sizable deviations from statistical distributions in di- to pentametallic lanthanide complexes have been reported by Kahwa and co-workers,[24c,e,g] but the exclusive characterization of these mixtures in the solid state prevents a rational assignment to specific short-range coupling mechanisms. For discrete oligomers, the unambiguous detection of intermetallic f−f mechanical coupling is difficult for ligand strands possessing different binding units, because deviations from the statistics (as observed for L36)[141] may originate from steric and/or electronic effects affecting one particular isomer. To the best of our knowledge, mechanical coupling in a discrete assembly has been established only for the triple-stranded helicate $[Ln_2(L26)_3]^{6+}$.[76a] Since L26 possesses C_{2v} symmetry, the two tridentate binding sites are equivalent. Speciation shows that the two homodimetallic $[Ln_2(L26)_3]^{6+}$ and $[Ln'_2(L26)_3]^{6+}$ and the heterodimetallic $[LnLn'(L26)_3]^{6+}$ helicates are the only significant species existing in solution upon stoichiometric mixing of L26 (3 eqs, $10^{-4}-10^{-2}$ mole·dm^{-3}) with $Ln(ClO_4)_3$ (1 eq) and $Ln'(ClO_4)_3$ (1 eq) in acetonitrile. For large Ln(III) (Ln = La−Eu), the expected statistical distribution is obtained (25% of each homodimetallic complex and 50% of the heterodimetallic), but the introduction of at least one smaller Ln(III) (Ln = Tb−Lu) induces deviations corresponding to $\Delta(\Delta G) \approx 4.2$ kJ·mol^{-1} (35% of each homodimetallic complex and 30% of the heterodimetallic).[76a] It was concluded that a small Ln(III) ion acts as a structural organizer which tightly wraps the ligand strands and favors the fixation of a second Ln(III) of similar size in the appended site via mechanical coupling.

V. Toward Programmed Functional Extended Networks

As seen above, dimetallic compounds exhibit a fascinating variety of unusual and programmable functional chemical properties. An obvious extension of these molecular objects is the design of polymetallic clusters, arrays, and aggregates while preserving the flexibility in programming their chemical, structural, and physicochemical properties. The tendency of lanthanide ions to adopt high coordination numbers and their ability to easily adapt to a given environment[3] make the design of mutidimensional arrays

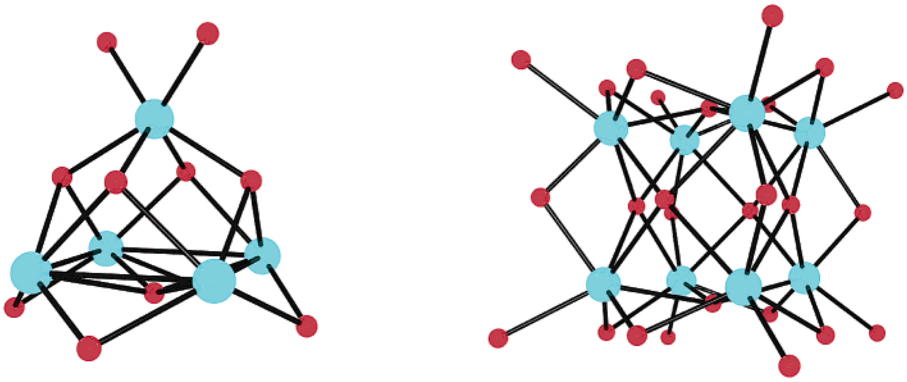


Figure 24. Eu- and O-atom array in $H_5[Eu_5O_5(L)_6(MeCN)_8]$ (left) and $H_{10}[Eu_8O_8(L)_{10}(O^iPr)_2(thf)_6]$ (right). (Drawn from data in ref 204.)

difficult. On the other hand, one may hope that introduction of these ions into networks possibly will result in unusual topologies. Several classes of rare-earth-containing polymetallic compounds are described, ranging from the inorganic superconductor copper–barium–yttrium oxides[192] to one-dimensional arrays containing Ln(III) and transition-metal ions as precursors for heterogeneous catalysts,[193] polymeric magnetic materials with double sheet[194] or ladder-type[74b] structures, compounds containing direct Ln–M bonds,[195] 3D luminescent coordination polymers,[196] lanthanide cluster receptors for the encapsulation of transition metals,[197] polymetallic complexes with a cubane-like cluster core,[58a] and fascinating supramolecular structures such as the recently reported "Lord of the rings" octameric self-assembled lanthanum wheel.[18b] The design of such edifices relies on (i) the bond-by-bond formation of linkages between the metal ions[195] or (ii) the introduction of bridging anions (iodides,[197] hydroxides,[18a] cycanides,[58a] chalcogenates,[198] salicylates,[199] carboxylates,[200] for instance) or polydentate ligands[196,201] or (iii) carefully planned self-assembly processes.[198,202] Although the functions of the final networks are usually not investigated and the description of these edifices is thus beyond the scope of this review, some potential stimulating applications can be envisioned. These supramolecular assemblies, generally characterized only in the solid state, appear as fascinating challenges for a rational structural and electronic programming of functions in extended polymetallic complexes. Selected examples are discussed below, but we do not intend to provide a comprehensive review of all the published work.

A. Clusters

Clusters are finite polymetallic entities, and their interest lies in several application fields, since they may be used as precursors for functional materials, ceramics, catalysts, and thin-film coatings. The latter are often obtained by converting alkoxide compounds to oxides via sol–gel techniques, a reason alkoxides clusters have drawn attention since they may give a clue to how metal oxide materials form. An early example in rare-earth chemistry stems from the laboratory of Evans, who investigated the transformation of a trimetallic yttrium alkoxide into a tetradecametallic cluster[203]

$$1\text{ equiv }YCl_3 + 2\text{ equiv }Na(OCMe_3) \rightarrow Y_3(OCMe_3)_7Cl_2(thf)_2\ (\text{yield} = 80\%) \tag{20}$$

$$Y_3(OCMe_3)_7Cl_2(thf)_2 \rightarrow [Y_7(OCMe_3)_{14}Cl_5O(thf)_2]_2\ (\text{quantitative}) \tag{21}$$

The resulting dimer has an inversion center and is comprised of four trimetallic $[Y_3(\mu_3\text{-}O(CMe_3)_3)\ (\mu_3\text{-}X)(\mu\text{-}Z)_3]$ (X = Cl, O; Z = Cl, $OCMe_3$) subunits connected by bridging entities: two chloride ions, one oxo anion, and a $[(\mu\text{-}O(CMe_3)_3)_2Y(\mu\text{-}Cl)]_2$ group. The same author has also shown that the reaction of europium metal with 2-propanol and 2,6-dialkylphenols (L) gives rise to complicated mixtures of products of which square-pyramidal Eu_5 and cubic Eu_8 clusters could be recrystallized in low yield: $H_5[Eu_5O_5(L)_6(MeCN)_8]$ and $H_x[Eu_8O_6(L)_{12}(O^iPr)_8]$.[204] Milder reaction conditions lead to different clusters, in particular the mixed-valence Eu(III)/Eu(II) compound $H_{10}[Eu_8O_8(L)_{10}(O^iPr)_2(thf)_6]$. However, the conditions for generating these edifices under controlled synthetic conditions remain to be found. The schematic arrangement of the Eu and O atoms is shown in Figure 24. Hybrid organic–inorganic materials (see also below) present a large diversity of application in materials sciences. In particular, compounds with polymerizable ligands are presently attracting attention. Within this scope, a nonametallic yttrium cluster has been obtained by reacting yttrium nitrate and the sodium salt of allyl acetatoacetate.[205] However, here again, stereochemical control is not achieved and different crystallization methods give rise to different structures.

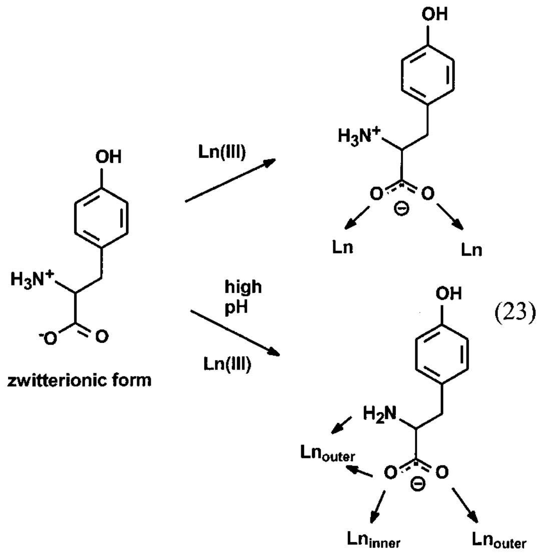
Another class of clusters are those generated by chalcogenolates in which the donor atom is either a sulfur or selenium atom. They are being extensively investigated by Brennan and co-workers, and we shall only cite one example here, the octametallic sulfido clusters $Ln_8S_6(SPh)_{12}(thf)_8$ which represents the most frequently observed cluster structure.[206,207] A cube of Ln atoms is connected by S^{2-} ligands capping its faces, with PhS^- ligands bridging the cube edges

$$8Ln(SPh)_3 + 6S + 8\ thf \rightarrow Ln_8S_6(SPh)_{12}(thf)_8 + 6\ Ph_2S_2 \quad \text{(in thf, at room temperature, high yield)} \qquad (22)$$

This cluster is invariant throughout the lanthanide series Ce–Er, and a potential application for the Ce cluster is the replacement of Hg-based pigments.

B. Self-Assembled Supramolecular Polymetallic Edifices

Controlled self-assembly of polymetallic lanthanide oxo and/or hydroxo complexes has recently been achieved by reacting lanthanide ions with α-amino acids.[58a,179] The driving force for this work is the possibility of developing synthetic nucleases able to hydrolyze DNA or RNA by cleaving phosphodiester bridges. Cubane-like tetrametallic clusters $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ are common motifs in this type of chemistry. Bridging individual cluster units by specific ligands may lead to the formation of three-dimensional networks or of specific receptors. For instance, the reaction of L-glutamic acid on erbium perchlorate followed by a strict control of the pH until precipitation begins yields a 3D porous network of discrete $[Er(\mu_3\text{-}OH)_4]^{8+}$ units and cluster-linking glutamate ligands. The overall structure features a 4.4 × 9.1 Å channel.[179] The use of tyrosine (Tyr), which may have different coordination modes to Ln(III) ions as depicted in eq 23, and the addition of a templating anion results in the self-assembly of specific anion receptors. One example is $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_{12}(\mu_2\text{-}H_2O)_5(H_2O)_8]^{12+}$,[208] the core of which contains five cubane-like Eu_4O_4 units.



(23)

The Eu(III) ions have a three-layer arrangement, each parallel layer containing five Eu(III) ions located at the vertexes of nearly perfect pentagons (Figure 25). Bromide may be substituted by chloride, but the resulting edifice is less stable, while iodide results in the formation of an entirely different structure, proving that structural control can be tuned by the template agent.[179] More complex self-assembled structures have been obtained by reacting *p*-sulfonatocalix[4]arene with pyridine *N*-oxide and lanthanum nitrate. Two calixarenes coordinate to the Ln(III) ion through the sulfonate groups to form a C-shaped dimeric assembly; two pyridine *N*-oxide ligands are bound to the metal ion and also within the calixarene cavities. These entities then self-assemble into large spherical or tubular clusters.[202]

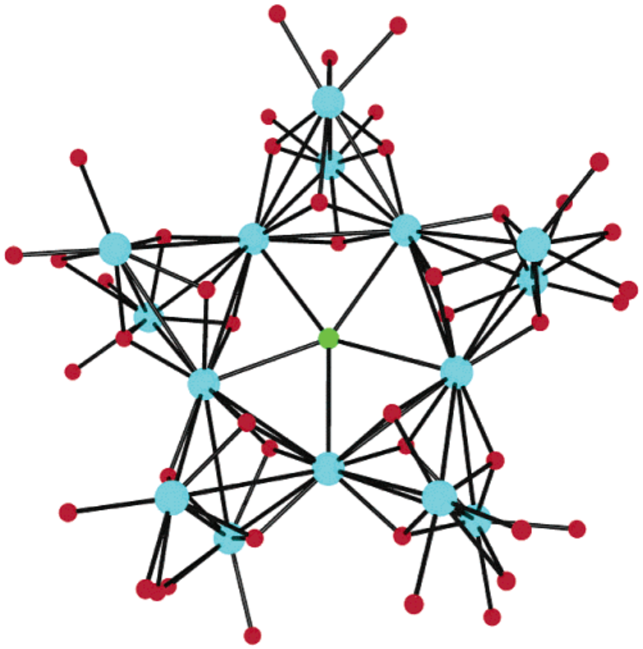


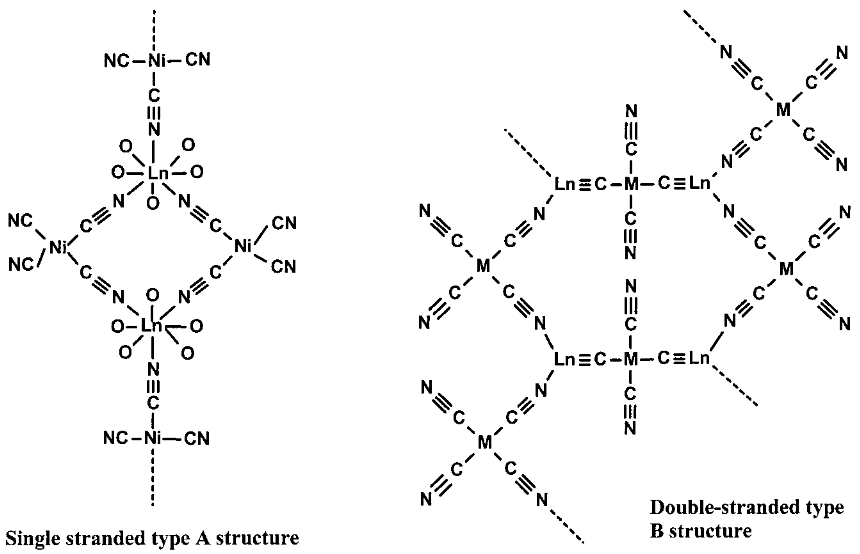
Figure 25. Structural core of the chloride receptor $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_{12}(\mu_2\text{-}H_2O)_5(H_2O)_8]^{12+}$. (Redrawn from ref 208.)

C. One-Dimensional Arrays

One of the earliest reports in this field describes rare-earth complexes with the general formula $Ln_2[Pt(CN)_4]_3{\cdot}xH_2O$ and adopting quasi-one-dimensional structures common to tetracyanoplatinate(II) compounds.[209] Similar compounds of the nickel triad (M = Ni, Pd, Pt) are easily obtained in dmf by means of simple metathesis reactions at room temperature[193]

$$2LnCl_3 + 3K_2[M(CN)_4] + 10\ dmf \rightarrow \{Ln_2[M(CN)_4]_3(dmf)_{10}\}_\infty + 6\ KCl \qquad (24)$$

In the corresponding structure for M = Ni (Figure 26), the one-dimensional array is generated by translating the repeating unit along the diagonals of the lattice, creating diamond-shaped Ln_2Ni_2 cores held together by the cyanide bridges (type A structure). Another motif is also obtained with M = Pd and Pt, i.e., a double-stranded zigzag chain (type B structure). These two structures have the same asymmetric units and the same repeating units but different combinations of the latter. In each case, the stereochemical control of the final structure is governed by the coordination around the lanthanide ion (distorted square antiprism).[193] Later, the same authors showed that a dimetallic Yb–Pd catalyst obtained by depositing $\{Yb_2[Pd(CN)_4]_3(dmf)_{10}\}_\infty$ on a


Single stranded type A structure

Double-stranded type B structure

Figure 26. Molecular structure of a one-dimensional array featuring nickel and lanthanide ions (only the O atoms from the dmf molecules are shown in structure A, while they are omitted in structure B, for the sake of clarity). (Redrawn from ref 193.)

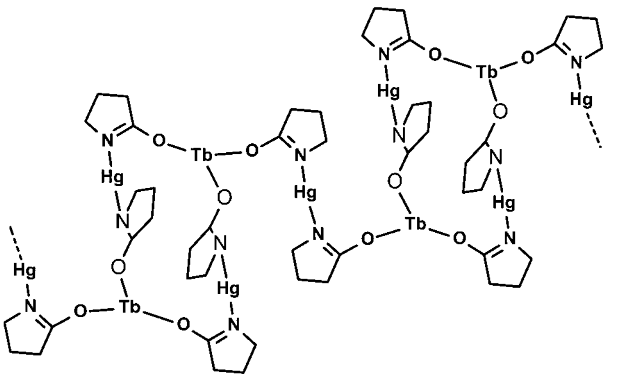
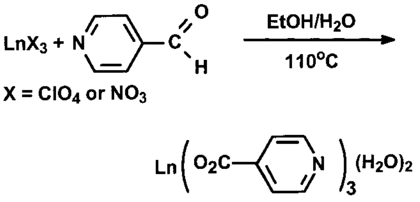


Figure 27. Schematic representation of the polymeric chain compound $\{[Hg_3Ln_2L_6(NO_3)_6]\}_\infty$ (Ln = Gd). (Redrawn from ref 212.)

titania surface is quite effective for the reduction of NO by methane in the presence of oxygen.[210] In addition, they demonstrated that the structural type B can also be obtained for the Ni(II) arrays and that type A can be interconverted into type B, which is thermodynamically favored. However, no rational explanation for the better stability of the latter is presently at hand.[211] A similar stereochemical control from the Ln(III) ion coordination requirements is seen in the polymeric compounds developed by Goodgame and co-workers and obtained by reacting lanthanide nitrates with the mercury salt of 2-pyrrolidone HgL_2, $\{[Hg_3LnL_4(NO_3)_3]\}_\infty$ (Ln = La−Gd) and $\{[Hg_3Ln_2L_6(NO_3)_6]\}_\infty$ (Ln = Tb−Yb).[212] Here the polymeric chains involve 16-membered macrocycles: the Hg(II) ions are connected to two 2-pyrrolidone ring N atoms, and the almost linear L−Hg−L entities bridge adjacent Ln(III) centers. In the Eu(III) compound, the 16-membered macrocycles interlock at the metal center, while in the Tb(III) polymer, an additional L−Hg−L unit links the macrocycles (Figure 27). An explanation lies in the smaller ionic radius of the Tb(III) ion, which results in fewer sterically demanding 2-pyrrolidone moieties being coordinated to this ion (three vs four for Eu). Moreover, there are interchain links between nitrate ions in one polymeric chain and Hg(II) cations in the next, so that the network here can be considered as being two-dimensional. Similar reactions with 2-oxazolidone lead to the formation of arrays containing contiguous fused 16- and 48-membered cycles.[213]

Luminescent one-dimensional lanthanide coordination polymers with formula $[Ln(isonicotinate)_3(H_2O)_2]$ have been obtained under hydrothermal conditions and in which the pyridine nitrogen atoms of the isonicotinate groups do not coordinate to the metal centers; instead, they direct the formation of Ln(III) coordination polymers via hydrogen bonding with coordinated water molecules (eq 25).



(25)

Again two different structures are evidenced: (i) a chain structure with Ce(III) centers alternately bridged by two and four carboxylate groups to adjacent Ce(III) ions and (ii) for Tb(III) a doubly carboxylate-bridged infinite-chain structure with one chelating carboxylate group on each metal center. When 4-pyridinecarboxaldehyde is replaced by benzaldehyde, no coordination polymer is obtained, which proves the directing role of the hydrogen bonds in the formation of the infinite chains. In both structures, the lanthanide centers also bind to two water molecules to yield an eight-coordinate, square antiprismatic geometry and the Eu(III) and Tb(III) polymers display an intense luminescence with efficiency equal to 8.6% and 90%, respectively.[200]

D. Two-Dimensional Arrays

Strictly speaking, ladder-type (or double sheet) arrays arise when a metal center has a connectivity in two directions. One example is the material

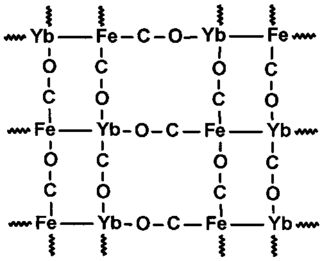


Figure 28. Schematic representation of the Yb−Fe sheet structure in $\{[(MeCN)_3YbFe(CO)_4]\}_\infty$. (Redrawn from ref 195.)

developed for the ferromagnetic coupling of Cu(II) with Gd(III), $[Gd_2(ox)][Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$, where ox stands for oxalato acting as a tetradentate bridging Gd···Gd ligand and pba for 1,3-propylenebis(oxamato), acting as an octadentate bridging ligand linking three metal ions Gd···Cu···Gd.[194] A puckered ladder-like arrangement of Gd[Cu(pba)]Gd units forms layers of a two-dimensional pattern connected by oxalato groups, while $[Cu(H_2O)_5]^{2+}$ aquo ions separate the layers. The specific design of this material was made in order to overcome limitations set to strong ferromagnetic interactions by one-dimensional chains with formula [MCu(pba)·solv]. Despite the relatively large Gd···Cu separation (≈5.7 Å), a sizable ferromagnetic interaction is detected between these two ions.

An organometallic ladder polymer with direct Yb−Fe bonds has been described by Shore and co-workers.[195] It is produced by reducing $Fe_3(CO)_{12}$ by Yb in liquid ammonia

$$3Yb + Fe_3(CO)_{12} + 6NH_3 \rightarrow 3(NH_3)_2YbFe(CO)_4 \qquad (26)$$

and crystallization at low temperature produces orange polymeric material with formula $\{[(MeCN)_3YbFe(CO)_4]_2\cdot x MeCN\}$ ($x = 0, 1$). The $YbFe(CO)_4$ units have a distorted trigonal-bipyramidal geometry around iron, while that of Yb(II) ions is a distorted octahedron. In the compound with $x = 1$, each Yb(II) ion is connected to two carbonyl oxygen atoms from two different $Fe(CO)_4$ units and each $Fe(CO)_4$ unit is connected to two different Yb(II) ions through isocarbonyl linkages, forming a zigzag chain; two chains are coupled to form a ladder through Yb−Fe interactions (Yb−Fe distance = 3.01 Å). The structure of the compound with $x = 0$ is closely related, but the polymeric ladders are cross-linked by Fe−CO−Yb isocarbonyl linkages to produce a sheet (Figure 28). When the crystals are redissolved, the presence of $HFe(CO)_4^-$ is detected, pointing to the rupture of the Yb−Fe bond in solution and demonstrating the crucial role of crystallization processes in the formation of extended polymetallic solid-state networks.

Polydentate aromatic N-donor ligands give a high degree of control over coordination frameworks. The hard oxygen-containing 4,4′-bipyridine-*N*,*N*′-dioxide, for instance, acts as a bridging ligand in the construction of 2D and 3D networks, the dimensionality being apparently determined by the size of the Ln(III) ions and, concomitantly, by its coordination number.[214] The 10-coordinate Sm(III) ion generates a 3D structure, while the 9-coordinate Er(III) ion leads to a 2D framework $\{[Er_2(NO_3)_6L_3]\cdot 2MeOH\}$. This framework belongs to a rather unusual topology (4.8^2), not yet observed in coordination chemistry, consisting of three connected nodes common to a tetragonal square unit and two octagons (Figure 29). The latter are 88-membered rings of ca. 2.6 nm diameter with 8 metal ions and 8 ligands. Interpenetration leading to a 3D network is prevented by four-membered ring motifs of adjacent layers occupying the large cavities.

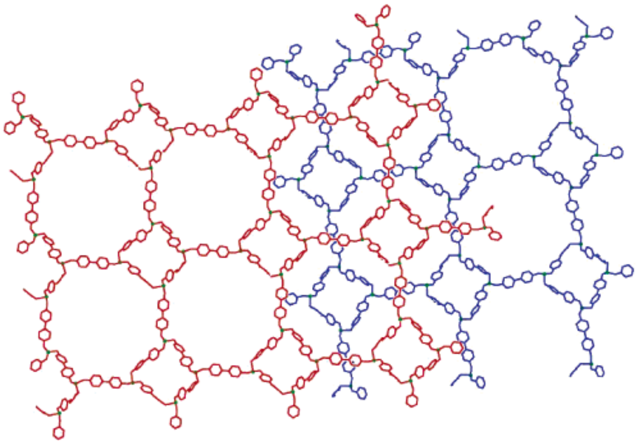


Figure 29. Two-dimensional grid with 4.8^2 topology formed by $\{[Er(NO_3)_6L_3]\cdot 2MeOH\}_\infty$. Two adjacent layers are shown in different colors. Nitrate groups, solvent molecules, and hydrogen atoms are omitted for clarity. (Reprinted with permission from ref 214. Copyright 2000 Royal Society of Chemistry.)

E. Three-Dimensional Arrays

Simple bridging ligands may also lead to 3D polymers, as in $\{[Sm(NO_3)_3L_2]\cdot 0.5H_2O\}_\infty$ (L = 4,4′-bipyridine-*N*,*N*′-dioxide), which has a distorted $CaSO_4$-like structure with a connectivity of four.[214] The same ligand induces another type of 3D network with the large La(III) ion and bulky tetraphenylborate anions, $\{[LaL_{2.5}(MeOH)(Ph_2B(OMe)_2)](BPh_4)_2\cdot 4.5MeOH\}_\infty$ (the $Ph_2B(OMe)^-$ anion results from the methanolysis of BPh_4^-). The resulting connectivity of five is unusual, and the compound possesses two kind of channels, square La_4 and rectangular La_8 ones. This product, however, only crystallizes as the minor component of the mixture, the major species being a 2D polymer $\{[La_4Cl_3L_{10}(MeOH)_{10}](BPh_4)_8Cl\cdot 22MeOH\}_\infty$ also featuring La(III) ions with a connectivity of five.[14c] That Ln(III) ions may easily build two different architectures from a common reaction mixture is inherent to the “chameleon” behavior of these ions with respect to coordination environments and makes the planning of specific motifs difficult. An application of three-dimensional lanthanide-containing arrays is in the field of thin-film electroluminescent devices which are often fabricated using the spin-coating technique. To achieve the appropriate spin-coating solution, Seward and co-workers used 4,4′-bipyridine (4,4′-bipy) and benzoic acid and found that it contains two coordination polymers, $\{Tb(O_2CPh)_3(MeOH)_2(H_2O)\}_\infty$ as a one-dimensional array and $\{Tb_2(O_2CPh)_6(4,4'bipy)\}_\infty$ as a 3D grid. Although the authors failed to demonstrate electroluminescence, the resulting films proved to be highly luminescent and the good film-forming properties of the solution were attributed to the presence of these polymeric structures.[196] The assembly of metal–organic frameworks (MOF) with microporous structure having accessible metal sites can be achieved from organic and inorganic building blocks. 1,4-Benzenedicarboxylic acid, H_2bdc, which is a dimonodentate ligand, reacts with Tb(III) nitrate under hydrothermal conditions, in the presence of triethylamine, to give an insoluble complex with formula $[Tb_2(bdc)_3(H_2O)_4]$ and extended 3D structure.[215] The central motif is parallelepiped having a Tb(III) ion at the center of its eight corners and bdc^{2-} on four of its faces. Other bdc^{2-} anions create the condensed network. The 8-coordination of the Tb(III) ion is completed by water molecules, an essential feature of the structure. Indeed, these molecules point in the parallelepiped. Subsequent thermal treatment removes the water molecules, creating a microporous material with 1D channels along the crystallographic *b*-axis. This leaves accessible metal sites that are potential luminescent probes for the assay of small molecules. Modified synthetic conditions, namely, methanol/dmf instead of water and pyridine, instead of triethylamine produce $[Tb(bdc)(NO_3)\cdot 2dmf]$, which upon desolvation yields a zeolite-like framework capable of reversible molecular sorption, for instance of CO_2.[216] The porosity of these open frameworks may be controlled by using the concept of secondary building units (SBU). For instance, polymerization of 4,4′-azodibenzoate (adb) with terbium nitrate in dmso containing triethylamine results in a 3D extended structure $\{[Tb_2(adb)_3(dmso)_4]\cdot 16dmso\}_\infty$ constructed from $Tb_2C_6O_{12}$ secondary building units (SBUs), each Tb(III) ion being bound to five adb linkers (four dimonodentate and one bidentate); 8-coordination is achieved by the binding of two dmso. The SBUs are joined together forming two interpenetrating networks with a large void space occupied by the 16 dmso guests. The 20 dmso molecules are lost upon heating at 180 °C; they can also be reversibly exchanged with other molecules such as $CHCl_3$ or dmf.[217] Another strategy to produce multifunctional porous materials starts from large molybdenum oxide species with transferable building blocks allowing a control of their size, like in the giant ring formed by $Na_6\{Mo_{120}O_{366}(H_2O)_{48}H_{12}[Pr(H_2O)_5]_6\}\cdot 200H_2O$. These materials have a variety of reaction centers, opening the way for the design of catalysts and for the study of magnetic and electronic interactions.[218]

VI. Outlook

In this review we have tried to illustrate how the combination of at least one 4f-block ion with other metal ions in molecular finite or supramolecular discrete architectures contributes (i) to enhance chemical or physical properties of the corresponding edifices and (ii) to create new functionalities emerging from orbital overlap, electrostatic interaction, or mechanical coupling between the metal centers. The major challenge pertaining to the elaboration of polymetallic assemblies containing f-elements resides in the coordination versatility of these ions which renders difficult a specific recognition. Elaborate tools are however emerging, taking advantage of modern molecular programming and, particularly, self-assembly processes, allowing us to plan the specific recognition of a d and a f element, for instance, or of two different f cations. Whenever possible, weak interstrand interactions or H-bonds may also help in organizing the receptor.[110] As an example, the stereochemical requirements of a d-transition-metal ion may be taken advantage of to facially preorganize ligands strands. The latter then form more easily an adapted receptor for the f-element, resulting in the specific and quantitative formation of the planned 3d–4f helicates, despite the wealth of potential other species that could form in solution.[5] In the absence of such a drive, e.g., when designing 4f–4f heterodimetallic species, more subtle chemical differences are involved between the two ions, requiring a much finer tailoring of the receptor. The major success of the past years has been to induce the formation of thermodynamically stable species by strict self-assembly in solution, whose structural features are maintained in the solid state.

The fascinating expansion of lanthanide coordination chemistry and supramolecular chemistry observed during these past two decades has been triggered by practical successes in catalysis, biomedical analysis, diagnostic, and, possibly, therapeutic medicine. The intrinsic chemical (Lewis acidity), magnetic, and spectroscopic (mainly luminescence) properties of these ions, often not matched by those of other transition-metal ions, make lanthanide ions privileged partners for the design of functional molecular entities and materials, especially now that these ions are available in high purity at a quite affordable cost. The basic properties of lanthanide ions have been known for a long time, but through the emergence of new polymetallic s–f, d–f, or f–f programmable molecular or extended edifices, it becomes evident that a good control of the inner coordination sphere may lead to predetermine changes in these properties. Moreover, longer range interactions either with species in the second coordination sphere or, better, with neighboring metal ions often result in the exaltation of specific properties. This opens the way to the synthesis of analytical sensors based on magnetism or luminescence and to tools such as molecular magnets, magnetic d–f switches, or directional light converters.

The future of lanthanide-containing polymetallic functional edifices appears bright, especially since a more rational command of a combination of modern synthetic tools (lock-and-key and induced fit principles, self-assembly, and self-organization) seems to be within reach to better plan the coordination environment of each ion and, also, its specific recognition. Although the design of extended lanthanide-containing polymetallic frameworks is still in its infancy (only limited rational programming and functions are currently accessible), highly convergent synthetic protocols using the simultaneous assembly of relatively simple building blocks leads to facile and rapid formation of the desired product with relatively low cost and effort. This methodology, combined with the use of strong coordination bonds, should lead to the formation of nanoscopic supramolecular edifices of predetermined shape and geometry and bearing the required functionalities. Examples of this trend is the coming out of metal−organic frameworks based on the linking, and cross-linking, of relatively large building units to yield microporous materials with interpenetrating networks. The building block approach is allowing molecular structural and reactivity properties to be translated into the new extended structures. One difficult aspect of this approach is the lack of detailed studies on the exact mechanism leading to the extended networks from the molecular precursors so that too often, despite the efforts of the chemists, minute changes in the initial reactant mixture result in very different topologies and structures. There is however no doubt that substantial improvements will be made in the future toward a better understanding of these phenomena.

VII. Acknowledgments

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